THE SYNTHESIS AND STUDY

of

POLYCYCLIC AROMATIC SYSTEMS.

THESIS

presented by

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for the Degree of

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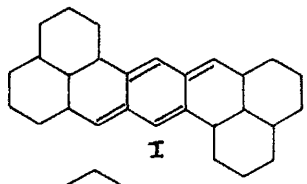
Chemistry Department,
University of Glasgow,
Glasgow, W., 2.

December, 1962.

CONTENTS.

SUMMARY.

A comparative study is made of the properties and reactions of the two isomeric hydrocarbons, 7,15-dihydroheptazethrene and 1.14,11.12-dibenzo-5,7-dihydropentacene. A similar investigation is carried out on hydro-derivatives of 5.6-dibenzozethrene and 1.2,4.5,6.7-tribenzotetracene. A chloro-derivative of 5.6,12.13-dibenzozethrene is synthesised. The behaviour of heptazethrene (I) and 5.6-benzozethrene (III) as normal aromatic hydrocarbons and the failure to observe any compound which could have the carbon skeleton of either 1.14,11.12-dibenzopentacene (II) or 1.2,4.5,6.7-tribenzotetracene (IV) are explained by the latter two compounds having no Kekulé structure, while the single Kekulé structures of heptazethrene (I) and 5.6-benzozethrene (III) are considered sufficient to ensure normal aromatic character.



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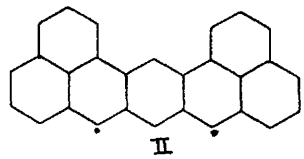

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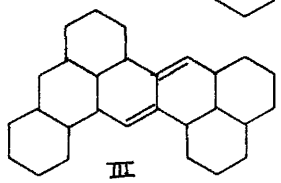

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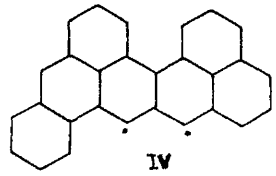
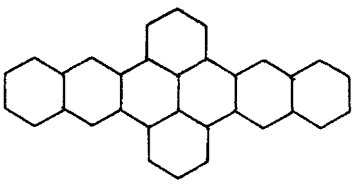


IV

Dinaphtho-(2'.3':1.2), (2".3":6.7)-pyrene (V), anthraceno-(2'.3':1.2)-pyrene (VI) and 1.14,4.5, 9.10,13.14-tetrabenzoheptacene (VII) are synthesised. The absorption spectra of these hydrocarbons are discussed with relation to other benzologues of pyrene and electronic structures are proposed for hydrocarbons of this type.



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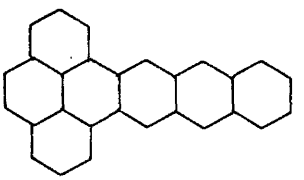

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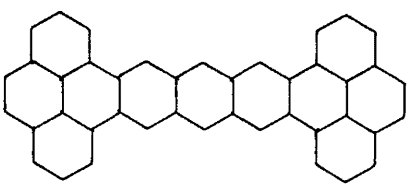
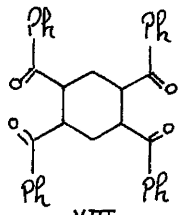


VII

The reduction of 1,2,4,5-tetrabenzoylbenzene (VIII) with copper powder in sulphuric acid is investigated with a view to the possible preparation of a compound having a bond of the Dewar type. The major product is found to be 5,6-dibenzoyl-1,3-diphenylisobenzofuran (IX). The azine derivative of this diketone (X) is found to be closely related

to 1,3-diphenyl-2',3'-isonaphthofuran (XI), which is obtained by reduction of 2,3-dibenzoylnaphthalene (XII). XI is the first example of a compound containing the 2,3-naphthoquinonoid system.



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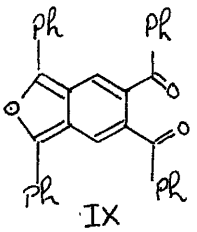

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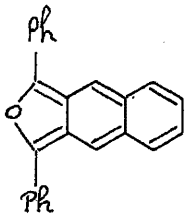

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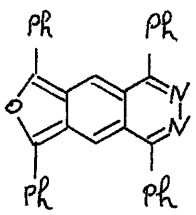

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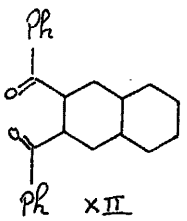


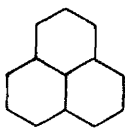
XII

S E C T I O N 1.

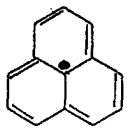
ZETHRENES.

The quantum-mechanical approach to the understanding and prediction of the stability of aromatic systems in the first place assumes the distribution of the π electrons over the whole ring system in molecular orbitals. This method does not require that, for stability, an aromatic system should be capable of being written in a classical form, i.e. having at least one Kekulé structure. Considerable interest therefore has been shown in the possible synthesis of a hydrocarbon which would be predicted to be stable by considering that the electrons belong to molecular orbitals, but which could not be described by a Kekulé structure.

Structure (1), $C_{13}H_9$, cannot be written with a Kekulé structure and in agreement with this the existence of (1) as the perinaphthyl radical (2) has been proved by paramagnetic measurements[1].



(1)



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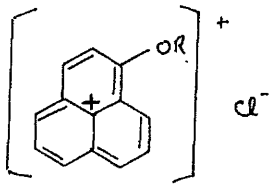
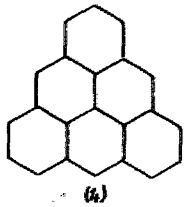


(3)

The readiness with which the cyclic polyenic frame is formed is illustrated by perinaphthenone which reacts with acid chlorides forming salts such as (3).

Structure (1), however, has an odd number of carbon and hydrogen atoms and could not possibly, under any scheme, have a complete set of paired electrons. In triangulene (4), $C_{22}H_{12}$ there are even numbers of carbon and hydrogen atoms. Also triangulene cannot be given a Kekulé structure. It therefore seemed likely that triangulene would provide an excellent test molecule since, from the standpoint of quantum mechanics, the four electrons in the centre of structure (5) might be arranged in pairs in molecular orbitals. A similar atomic arrangement exists in methylene-cyclopropene (6)[2].



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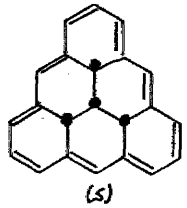
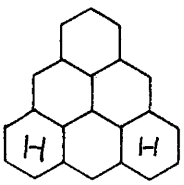


(5)

(6)

The first prediction of the instability of triangulene was made by Clar[3]. This prediction was later confirmed by synthetic work by Clar and Stewart[4] when they found that hexahydrotriangulene (7) failed to give the parent aromatic system when

dehydrogenated under conditions which had been applied successfully to very reactive aromatic hydrocarbons such as hexacene. They found also that, although reduction of triangulenequinone (8) with alkaline sodium dithionite solution gave a coloured solution which looked like a vat, this was not derived simply from the hydrocarbon but had the structure (9).



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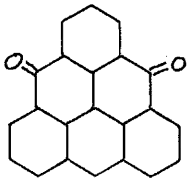

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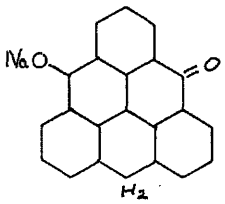
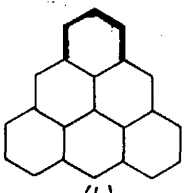


(9)

A hydrocarbon isomeric with triangulene is anthanthrene (10). Like triangulene (5), anthanthrene can be written with a frame of alternating double bonds enclosing four electrons (11). Unlike triangulene, however, anthanthrene behaves like a normal aromatic hydrocarbon.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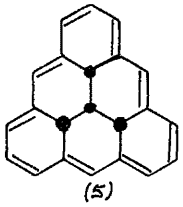
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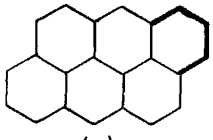
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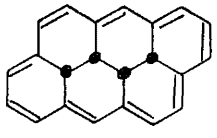
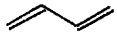

(11)

If the frame of double bonds is neglected the difference between triangulene and anthanthrene is reduced to the difference between (12) and (13). In (13) the electrons can be paired resulting in the classical structure of butadiene (14). In (12) the electrons cannot be paired to give two double bonds and methylenecyclopropene (6) obviously cannot replace two double bonds in an aromatic system.

(12)

(13)

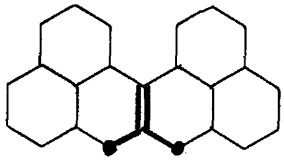
(6)



(14)

Isomerism of this type is also shown by dibenzotetracene (15) and zethrene (16). In zethrene the electrons can be paired forming double bonds as indicated. An interesting feature of zethrene is that only one Kekulé structure can be written for the central portion of the molecule. If only classical structures are used to describe the molecule the two double bonds in the central region are therefore fixed. Dibenzotetracene has no Kekulé structure and can only be formulated as a diradical, (15) or (17). This comparison of (12) and (13) is not intended to represent the

electronic conjugation in molecules such as (5), (11), (15) and (16); it is used merely to show that the same type of isomerism is present in both pairs.



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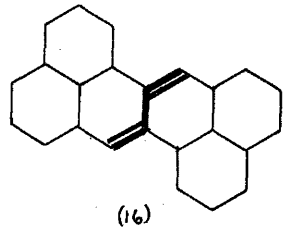

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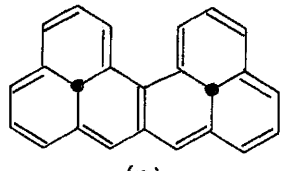
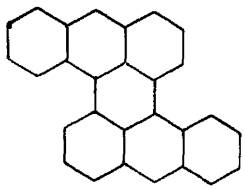


(17)

The synthesis of zethrene[5] has shown that, even though it contains two formally fixed double bonds, it behaves as a normal aromatic hydrocarbon. This is illustrated by the striking similarity in the absorption spectra and reactivity of zethrene (16) and dibenzoperylene (18) which has no fixed double bonds. Clar, Kemp and Stewart[6] attempted to investigate the stability of dibenzotetracene (15) by direct synthesis. However, great difficulty was experienced in the preparation of dibenzotetracenequinone (19) by cyclisation of dinaphthylmalonic ester (20) and related compounds.

Because of the very low yields of dibenzotetracene-quinone (19) the interest of Clar and his co-workers[6] was turned to the more readily accessible dibenzopentacenequinone (21).



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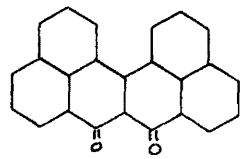

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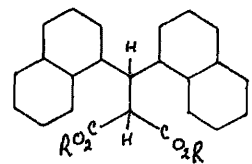

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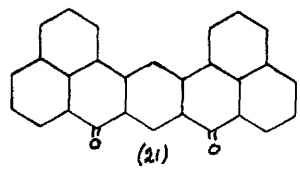
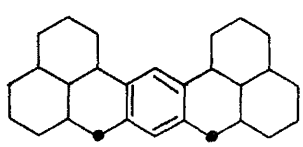


(21)

Dibenzopentacene (22) would serve the same purpose as dibenzotetracene (15) since it also can have no Kekulé structure. In agreement with their predictions Clar, Kemp and Stewart found that dehydrogenation of hexahydrodibenzopentacene (23) gave no evidence of the existence of dibenzopentacene as a normal aromatic hydrocarbon.



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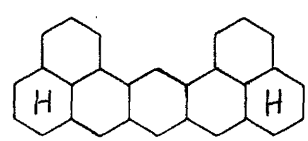
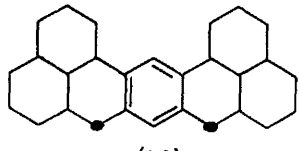


(23)

Isomeric with dibenzopentacene (22) is the previously undescribed heptazethrene (24) in which, like zethrene, the double bonds in the central region

must be fixed if only Kekulé structures are considered. In heptazethrene, however, there are four double bonds arranged across the centre of the molecule in a p-quinonoid system. Thus the isomerism in this case can be thought of as being similar to that of m- and p-xylylene (25) and (26).



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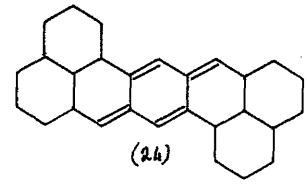

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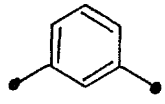

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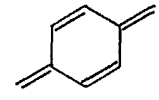
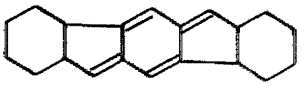


(26)

Although p-xylylene (26) has only one classical structure it has been isolated and shown to exist as a normal hydrocarbon (though a very reactive one) by its diamagnetism and by spectroscopic measurements. Its preparation and properties have been reviewed recently[7]. m-Xylylene (25) can have no Kekulé structure and no compounds incorporating this structure are known.

One of the simplest hydrocarbons having four fixed double bonds in the p-quinonoid structure would be (27). Although the parent

system is as yet unknown, various derivatives have been described. The quinone (28) forms a brilliant deep blue vat on reduction with alkaline sodium dithionite. The dihydro-compound (29), however, has remained resistant to dehydrogenation even in the vapour phase in contact with palladium-charcoal at 400° [8].



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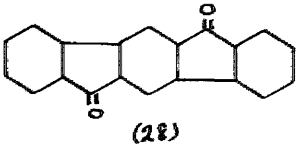

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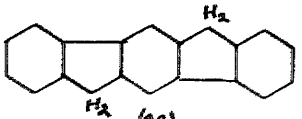
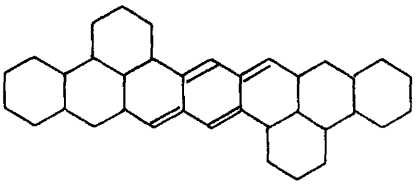


(29)

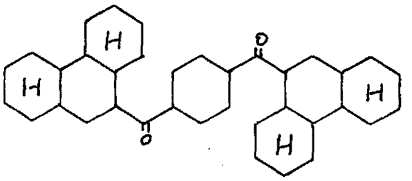
While it was known that hexahydrodibenzopentacene (23) did not give the corresponding dibenzopentacene on dehydrogenation, a direct comparison of derivatives of dibenzopentacene (22) and heptazethrene (24) was not available. Dibenzoheptazethrene (30) had been synthesised by Clar, Fell and Richmond[9] but since it contained two benzenoid rings more than heptazethrene[+] this

[+] The effect of benzenoid rings on the stability of aromatic hydrocarbons is discussed in Section 2.

compound was not suitable for a close comparison. Hydrogenated derivatives of dibenzoheptazethrene (30) were obtained by pyrolysis of the diketone (31).



(30)



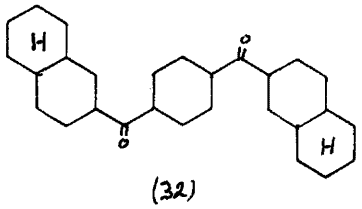
(31)

The need then was obvious for a comparative study of the properties of the isomers heptazethrene (24) and dibenzopentacene (22) and their derivatives.

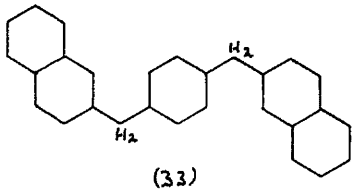
HEPTAZETHRENE AND 1.14, 11.12-DIBENZOPENTACENE.

HEPTAZETHRENE AND 1.14, 11.12-DIBENZOPENTACENE.

By analogy with the synthesis of dibenzoheptazethrene (30)[9], it was hoped to obtain the carbon skeleton of heptazethrene by cyclisation of 1,4-di(5,6,7,8-tetrahydronaphthoyl) benzene (32) under Elbs Reaction conditions. Crude diketone (32), obtained by Friedel-Crafts condensation of tetralin and terephthalyl chloride, was pyrolised at 470°. This temperature is somewhat higher than that required for a normal Elbs reaction but no charring was observed and water was evolved smoothly as the temperature rose from 380 to 470°.



(32)

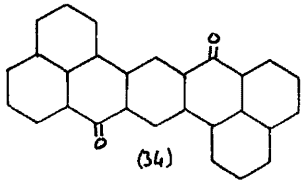


(33)

The only product obtained pure was a hydrocarbon, the properties of which suggest the compound 1,4-di-(naphthylmethyl) benzene (33). This would be in agreement with the findings of Orchin, Woolfolk and Reggel[10] who obtained 2-benzyl naphthalene from

β-benzoyltetralin under similar conditions. No compound with the expected properties of a hydrogenated derivative of heptazethrene could be isolated.

An unsuccessful attempt was made to obtain heptazethrenequinone (34) by cyclisation of 1,4-di-α-naphthoylbenzene (35) in an aluminium chloride melt. This reaction had been successfully applied to α-benzoylnaphthalene (36) by Scholl[11] in the synthesis of benzanthrone (37).



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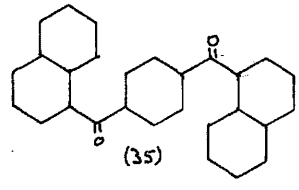

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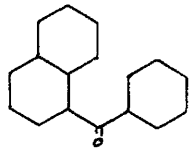

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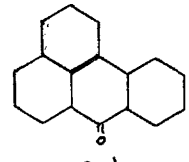
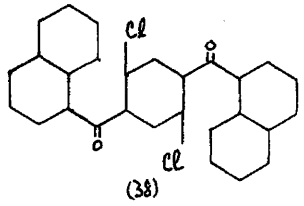


(37)

The only successful syntheses of heptazethrenequinone (34) was via 2,5-dichloro-1,4-di(α-naphthoyl) benzene, (38). Direct chlorination of p-xylene gave a mixture of products from which 2,5-dichloro-p-xylene was separated[12]. This was oxidised first with nitric acid and then with alkaline potassium permangate giving 2,5-dichloro-p-toluic acid and 2,5-dichloroterephthalic acid respectively. The

oxidation was carried out in the same manner as that used for the oxidation of 4,6-dichloro-m-xylene[13]. 2,5-Dichloroterephthalyl chloride was prepared by treatment of the acid with phosphorus pentachloride and was condensed in good yield with two molecular equivalents of naphthalene in methylene chloride by treatment with aluminium chloride.



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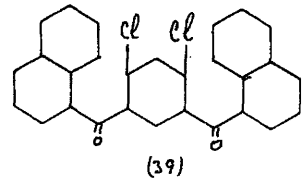

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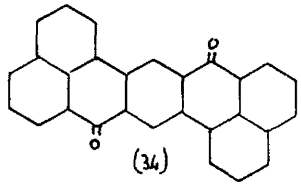

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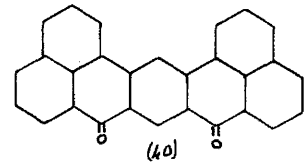
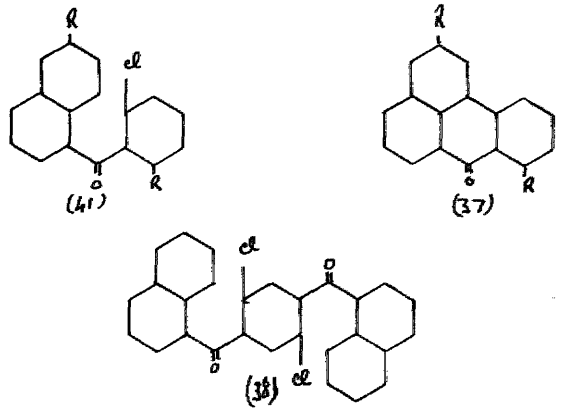


(40)

The isomeric diketone, 1,3-dichloro-4,6-di(α-naphthoyl) benzene (39)[13] has been cyclised to 1.14, 11.12-dibenzopentacene-5,7-quinone (40) by treatment with potassium hydroxide in quinoline and by fusion with an alcoholic solution of potassium hydroxide at 140°[6]. The latter method applied to (38) gave no quinone, only acidic material being produced. Treatment of the diketone with potassium hydroxide in boiling quinoline afforded heptazethrenequinone in low yield. Slight modifications, designed to promote greater dispersion

of the molten potassium hydroxide in the quinoline and hence to reduce the time required, were introduced, increasing the yield somewhat. The amount of potassium hydroxide used was critical, a slight excess causing a marked reduction in yield. Benzanthrone (37) and some of its derivatives were known to have been obtained by cyclisation of 1-(o-chlorobenzoyl) naphthalene (41) and related compounds with alkali metal salts at elevated temperatures[14]. This method was successfully applied to the diketone (38) although yields were poor.

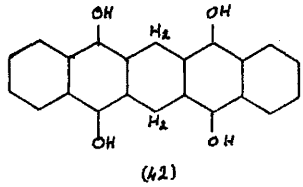


In both these cyclisations yields were low and inconsistent, variation occurring under apparently identical conditions.

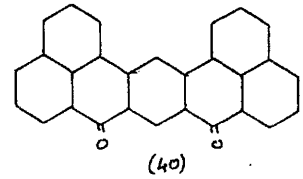
1.14,11.12-Dibenzopentacene-5,7-quinone (40) was synthesised using the method of Clar, Kemp and Stewart[6]. The modification introduced into the potassium hydroxide/quinoline cyclisation resulted

in a considerable increase in yield.

Having obtained the two quinones, (34) and (40), by analogous syntheses starting from p- and m-xylene respectively it is now possible to say that, when 5,14,12,8-tetrahydroxy-6,13-dihydropentacene (42) is reacted with glycerol and sulphuric acid[15], only 1.14,11.12-dibenzopentacene-5,7-quinone is formed and not heptazethrenequinone as was thought previously. This can readily be seen from Table I. The absorption spectra of the two quinones are shown in fig. I.



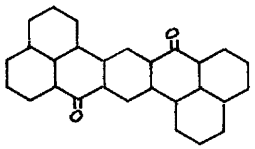
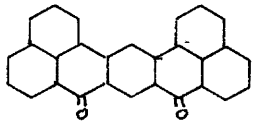
(42)



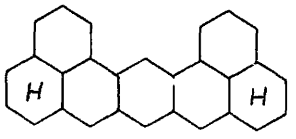
(40)

It has been reported[6] that dibenzopentacene quinone (40) could be reduced in poor yield by phosphorus and hydriodic acid to 1.14,11.12-dibenzo-2,3,4,8,9,10-hexahydropentacene (23). It has now been found, however, that reduction with zinc dust, pyridine and acetic acid proceeded smoothly affording 1.14,11.12-dibenzo-5,7-dihydropentacene (43). The same technique applied to the isomeric quinone (34) gave 7,15-dihydroheptazethrene (44), although in much lower yield. This hydrocarbon was also

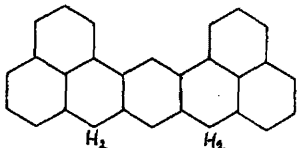
TABLE I.

Structure			Unknown, from (42)
M.P.	456°	435°	> 370°
Crystal Form	Orange-yellow needles from nitrobenzene	Yellow needles from nitrobenzene	Sublimes in orange-yellow needles
Sulphuric Acid	Bright green	Violet-red with red fluorescence	Red with orange-red fluorescence
Vat Formation	Formed a sparingly soluble blue vat	Did not form a vat	Did not form a vat
Absorption Bands	3230, 3340, 4190, 4420, 4705 Å In trichlorobenzene	3510, 4065, 4305 Å In trichlorobenzene	3530, 4080, 4320 Å In trichlorobenzene

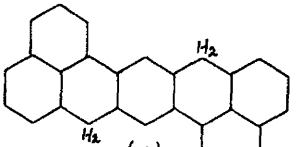
obtained by reduction of heptazethrenequinone with aluminium cyclohexoxide in cyclohexanol. Reduction of the quinone with phosphorus and hydriodic acid and by fusion in a zinc dust melt resulted in mixtures of more highly hydrogenated derivatives of heptazethrene.



(23)



(43)



(44)

The absorption spectra of the two isomeric dihydro-compounds are recorded in fig. II. They are very similar, as might be expected from two structures differing only in the substitution of a benzene ring. The reactions of the two hydrocarbons were, however, quite different. When dihydroheptazethrene was sublimed over palladium charcoal (prepared by the method of Newman and Zahn[16]) dark green material was observed in the neighbourhood of the catalyst. When sublimed clear of the charcoal, however, this material decomposed, the product being dihydroheptazethrene. When

dihydrodibenzopentacene (43) was sublimed on to palladium charcoal it was absorbed completely on it and no material could be sublimed from the catalyst, even at temperatures greater than 500°. The dibenzohexahydropentacene (23) is reported to behave in exactly the same manner[6].

Palladium charcoal could also be used to dehydrogenate dihydroheptazethrene at lower temperatures. When a solution of (44) in trichlorobenzene was heated with palladium charcoal in an evacuated ampule, a deep blood-red colour quickly developed and the solution showed the absorption bands of heptazethrene. As the solution cooled, the colour gradually faded leaving a pale yellow solution. Reheating the solution quickly restored the red colour and the spectrum of heptazethrene. This was later shown to be a property of heptazethrene itself and not just a fresh dehydrogenation of unreacted dihydroheptazethrene, when it was found that solutions of heptazethrene, under carbon dioxide and free from any dehydrogenating agent, showed the same phenomenon. A solution of dihydrodibenzopentacene (43) when treated with palladium charcoal at 200° gave only a gradual increase in the general absorption over

several days.

Chloranil dehydrogenated dihydroheptazethrene (44) in solution in warm benzene. When reacted quickly with a calculated amount of chloranil in concentrated solution, in boiling xylene, it formed a dark green precipitate soluble in benzene giving blood red solutions having the spectrum of heptazethrene. This precipitate decomposed on sublimation reforming dihydroheptazethrene. Dihydrodibenzopentacene (43) was unaffected by chloranil in boiling benzene, but in boiling trichlorobenzene it formed insoluble chlorine-containing material.

Dihydroheptazethrene was dehydrogenated in nitrobenzene solution at just below its boiling point. However if this temperature were maintained for more than a few minutes, or if the solution were boiled, oxydation occurred forming hepta-zethrenequinone (34).

Both hydrocarbons (43) and (44) reacted with bromine forming dark green precipitates. Dihydroheptazethrene (44) reacted with maleic anhydride giving alkali-soluble material which was cyclised in a zinc chloride melt to a red compound

whose absorption spectrum was typical of an aromatic hydrocarbon. Because of the scarcity of dihydroheptazethrene, however, it was not possible to investigate these reactions further. Dihydrodibenzopentacene (43) gave on prolonged reflux with maleic anhydride only an alkali insoluble tar.

Dihydroheptazethrene (44) was dehydrogenated and chlorinated by reaction with phosphorus pentachloride in boiling xylene. When the amount of phosphorus pentachloride was restricted the chloro-derivative obtained was blue and had absorption bands at 6000 and 5640 Å. When there was an excess of phosphorus pentachloride a green chloro-derivative was formed having absorption bands at 6260 and 5740 Å. Dihydrodibenzopentacene (43) also reacted with phosphorus pentachloride the product in this case, however, was completely insoluble in solvents such as boiling nitrobenzene.

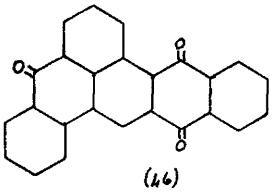
As with dibenzoheptazethrene[9] salts of heptazethrene could be obtained by treatment of solutions of the hydrocarbon with strong acids. These salts were insoluble in non-polar solvents but dissolved in acetic acid in the presence of the appropriate acid.

Solutions of heptazethrene (24) (from dihydro-heptazethrene (44) and chloranil) were purified for spectroscopic measurements by boiling with molten potassium hydroxide when any unreacted chloranil and by-products were removed. For measurement of the complete spectrum of heptazethrene (fig. III) several freshly prepared solutions were required.

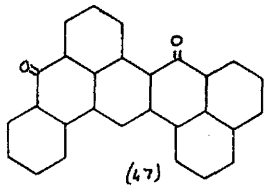
5.6-BENZOZETHRENE AND 1.2,4.5,6.7-TRIBENZOTETRACENE.

5.6-BENZOZETHRENE AND 1.2,4.5,6.7-TRIBENZOTETRACENE.

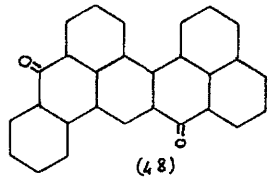
It has been shown recently by Vollmann[17] that "benzanthronisation" of the triketone (46) by treatment with glycerol and sulphuric acid gave a mixture of 5.6-benzozethrenequinone (47) and tribenzotetracenequinone (48). Since only benzozethrenequinone (47) formed a vat, separation could be achieved, although this method was not recommended for preparative work.



(46)



(47)



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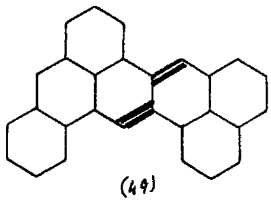
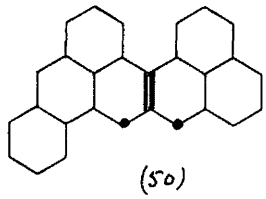


(49)

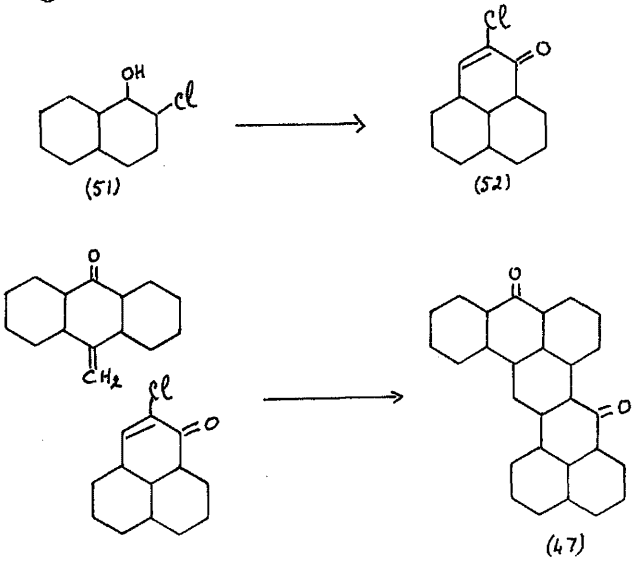


(50)

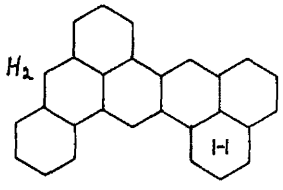
The two isomeric quinones (47) and (48) are derived from benzozethrene (49) and tribenzotetracene (50) respectively. Benzozethrene, like zethrene, has two fixed double bonds whereas tribenzotetracene has no Kekulé structure. Thus, as with heptazethrene and dibenzopentacene, a comparative study of the two isomers (49) and (50) would be of great

value in any discussion of the significance of Kekulé structures.

5.6-Benzozethrene-4,14-quinone (47) was prepared by a route indicated by Vollman[17]. α-Naphthol was chlorinated in alkaline solution with sodium hypochlorite giving 2-chloro-1-naphthol[18](51). By reaction of this with glycerol and sulphuric acid, 2-chloroperinaphthenone-1[19](52) was obtained which condensed with methyleneanthrone[20] in boiling nitrobenzene forming the quinone (47) in low yield. 2-Chloroperinaphthenone could be recovered in 50% yield from the condensation and the low yield would probably be caused by decomposition of the methylene-anthrone at the high temperature and under the acidic conditions produced by the evolution of hydrogenchloride.



The quinone (47) was reduced by zinc dust in pyridine and acetic acid in rather low yield to a tetrahydro-5.6-benzozethrene (53) or (54). It is not possible to say with any certainty from an examination of the ultra-violet spectrum (fig. IV) which of the two structures is correct. When it was sublimed over palladium charcoal[16] at 310° a deep blue glass was obtained. This, however, was very soluble and could not be crystallised, probably being a solid solution of 5.6-benzozethrene (49) in hydrogenated derivatives.



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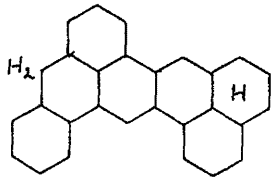
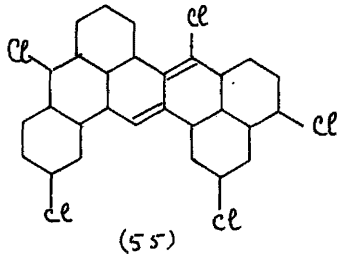


(54)

5.6-Benzozethrene formed a dark green salt with perchloric acid. Although rather unstable, this salt, if handled quickly, could be used to prepare relatively pure solutions of the hydrocarbon.

The tetrahydro-5.6-benzozethrene reacted with phosphorus pentachloride yielding a pentachloro-5.6-benzozethrene, possibly (55). This material

was very much more stable than benzozethrene itself and crystallised well. Its absorption spectrum is very similar to that of the parent hydrocarbon (fig. V).



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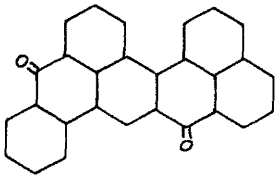

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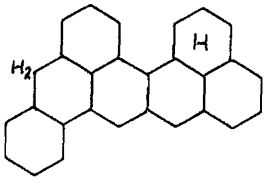

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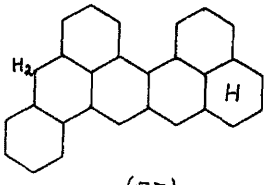


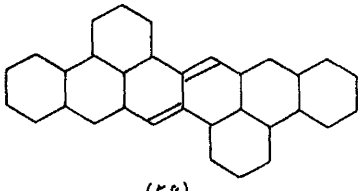
(57)

Zinc dust, pyridine and acetic acid reduced 1.2,4.5,6.7-tribenzotetracene-3,11-quinone (48)[21] to a tetrahydro-1.2,4.5,6.7-tribenzotetracene (56) or (57). As with the isomeric hydrocarbon no decision can be reached, from a study of its absorption spectrum (fig. IV), as to the positions of the hydrogen atoms. On sublimation over palladium charcoal at 300°, the hydrocarbon was completely absorbed on the catalyst. Treatment of a solution of the hydrocarbon with palladium charcoal at 200°

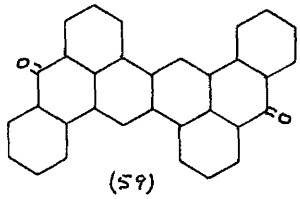
for 16 hours did not appear to effect any dehydrogenation.

5.6,12.13-DIBENZOZETHRENE.

Of the benzologues of zethrene (16), 5.6-benzozethrene (49), 4.5,11.12-dibenzozethrene (58)[6] and heptazethrene (24) have now been described. The quinone of 5.6,12.13-dibenzozethrene (59) is also known and the possibility of the preparation of 5.6,12.13-dibenzozethrene (60) is briefly investigated here.

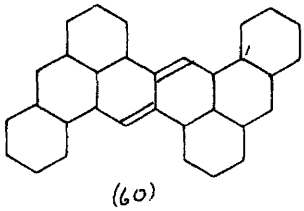


(58)

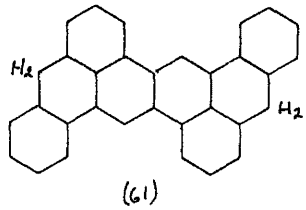


(59)

Dibenzozethrenequinone (59)[22] was reduced to dihydrodibenzozethrene (61) by treatment with zinc dust in pyridine and acetic acid. This hydrocarbon was readily reoxidised to the quinone (59). Although it could not be dehydrogenated to dibenzozethrene (60) with palladium-charcoal, it did react with phosphorus pentachloride to give a chloro-derivative of dibenzozethrene. The absorption spectrum of this chloro-derivative is shown in fig. VI.



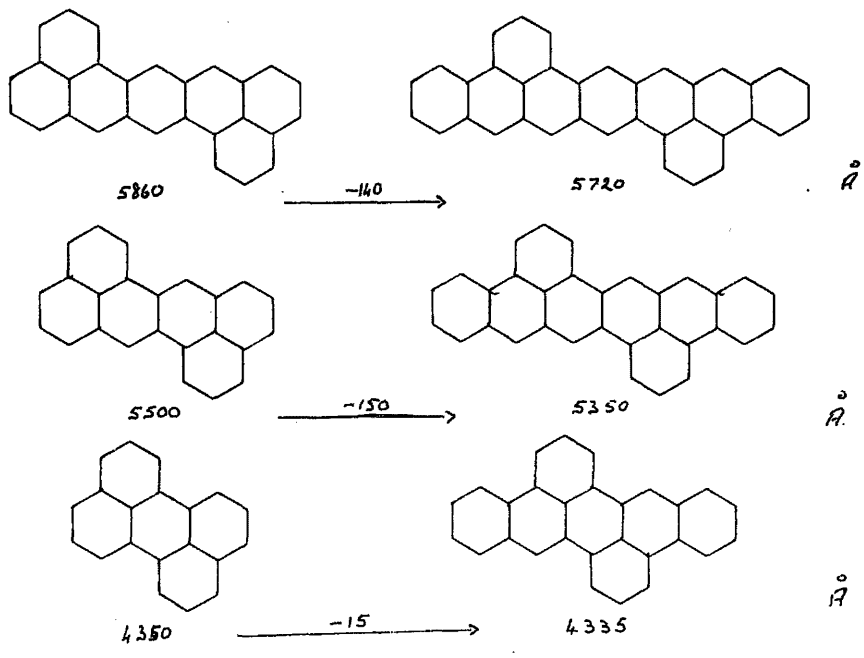
(60)



(61)

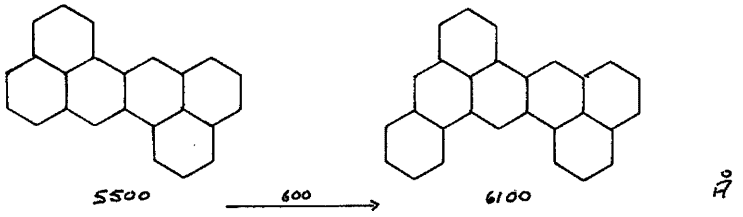
CONCLUSION.

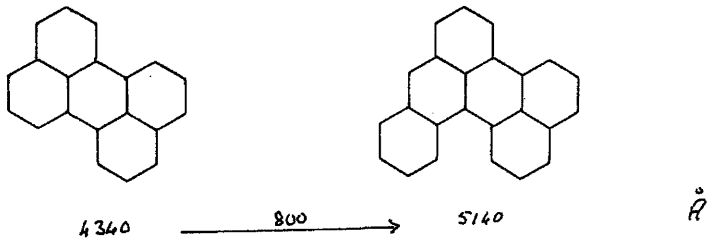
Heptazethrene (24) has been shown to exist as a normal aromatic hydrocarbon very similar to, though more reactive than, the related dibenzozethrene (30)[9]. This similarity is illustrated by a comparison of the absorption spectra of the two hydrocarbons (fig. III). The greater stability of dibenzoheptazethrene (30) is readily explained by the fact that this hydrocarbon has two benzenoid rings more than heptazethrene. This difference is also shown by the shift of the long-wave absorption bands to the violet when passing from heptazethrene (24) to dibenzoheptazethrene (30). Similar shifts have been recorded for zethrene (16) and dibenzozethrene (62)[6], and for perylene (63) and dibenzoperylene (64)[23].



This relationship between the stability of a hydrocarbon and the maximum number of benzenoid rings which it can possess is discussed further in the introduction to Section 2.

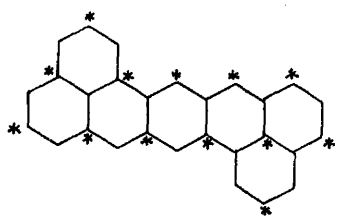
The shift in passing from zethrene (16) to benzozethrene (49) is of the same order as the shift in passing from perylene (63) to benzoperylene (65). In this case the shift is towards the red as would be expected, since no benzenoid ring is formed in the annellation.



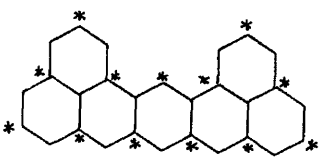


The difference between heptazethrene (24) and dibenzopentacene (22), and between benzozethrene (49) and tribenzotetracene (50) can be demonstrated in

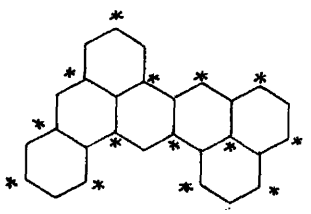
the following way.

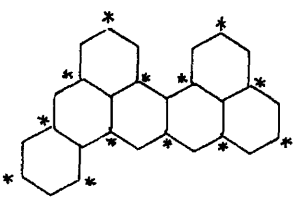


14 Starred
14 Unstarred



13 Starred
15 Unstarred

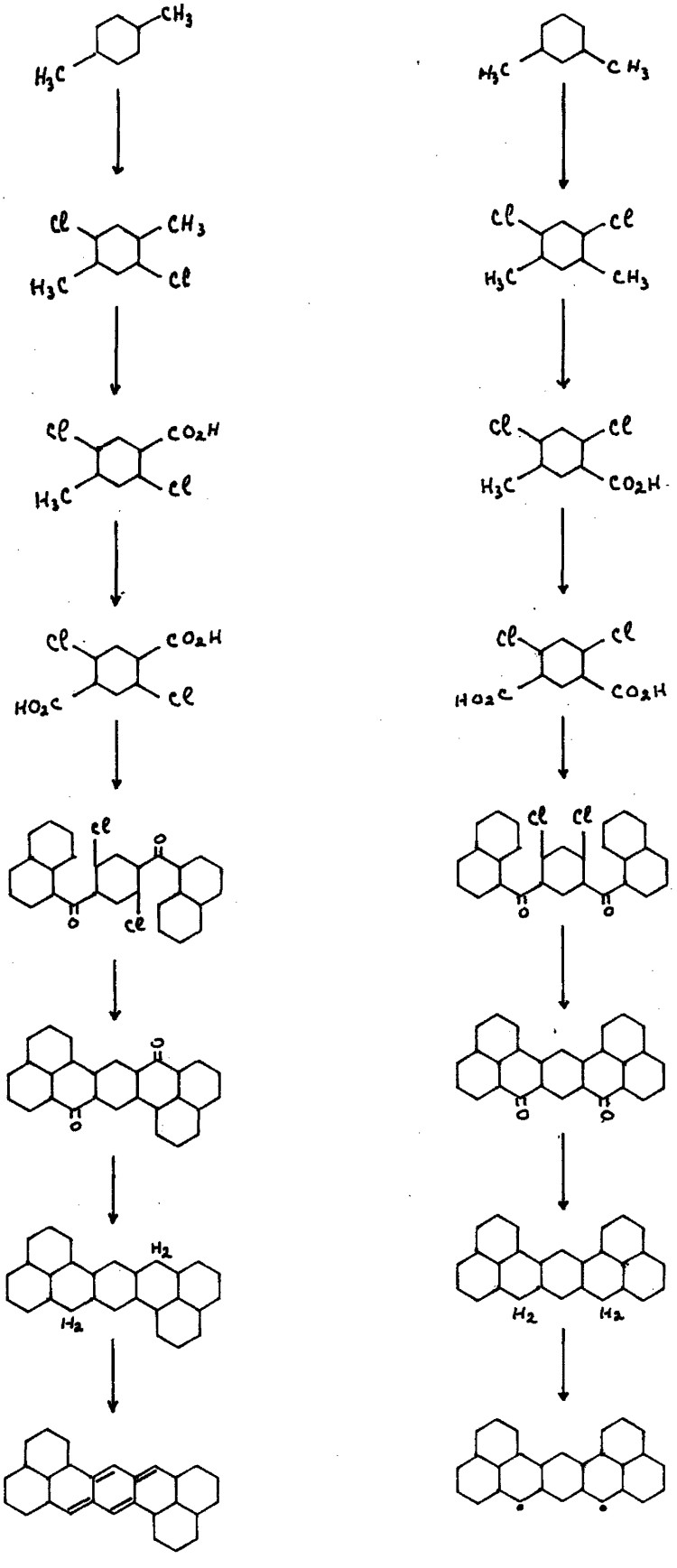




Although the above hydrocarbons are all alternant interms of the original definition[24] the numbers of starred and unstarred atoms are not equal in dibenzopentacene (22) and tribenzotetracene (50). If one pair of carbon atoms (one marked and one unmarked) is identified with a double bond, then it can be seen that only heptazethrene (24) and benzozethrene (49) can have a Kekulé structure.

Heptazethrene (24) and benzozethrene (49) have been shown to behave as normal aromatic hydrocarbons whilst their isomers have not been able to be prepared.

This is what would be expected if at least one Kekulé structure were necessary for the stability of an aromatic hydrocarbon.



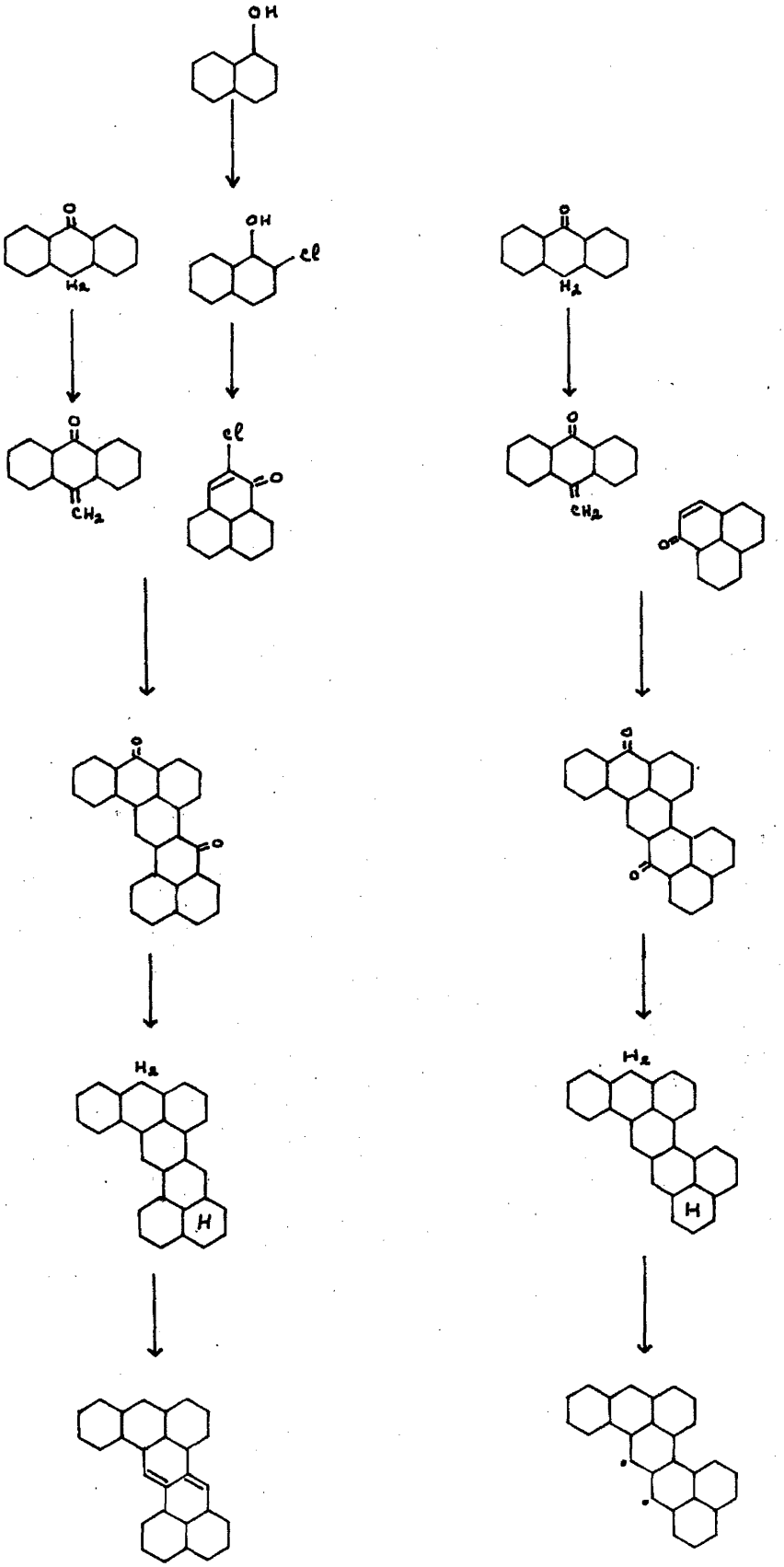

OH
O
H2
OH
Cl
O
CH2
Cl
O
O
H2
O
CH2
O
O
O
O
H2
H
H2
H

Fig. I

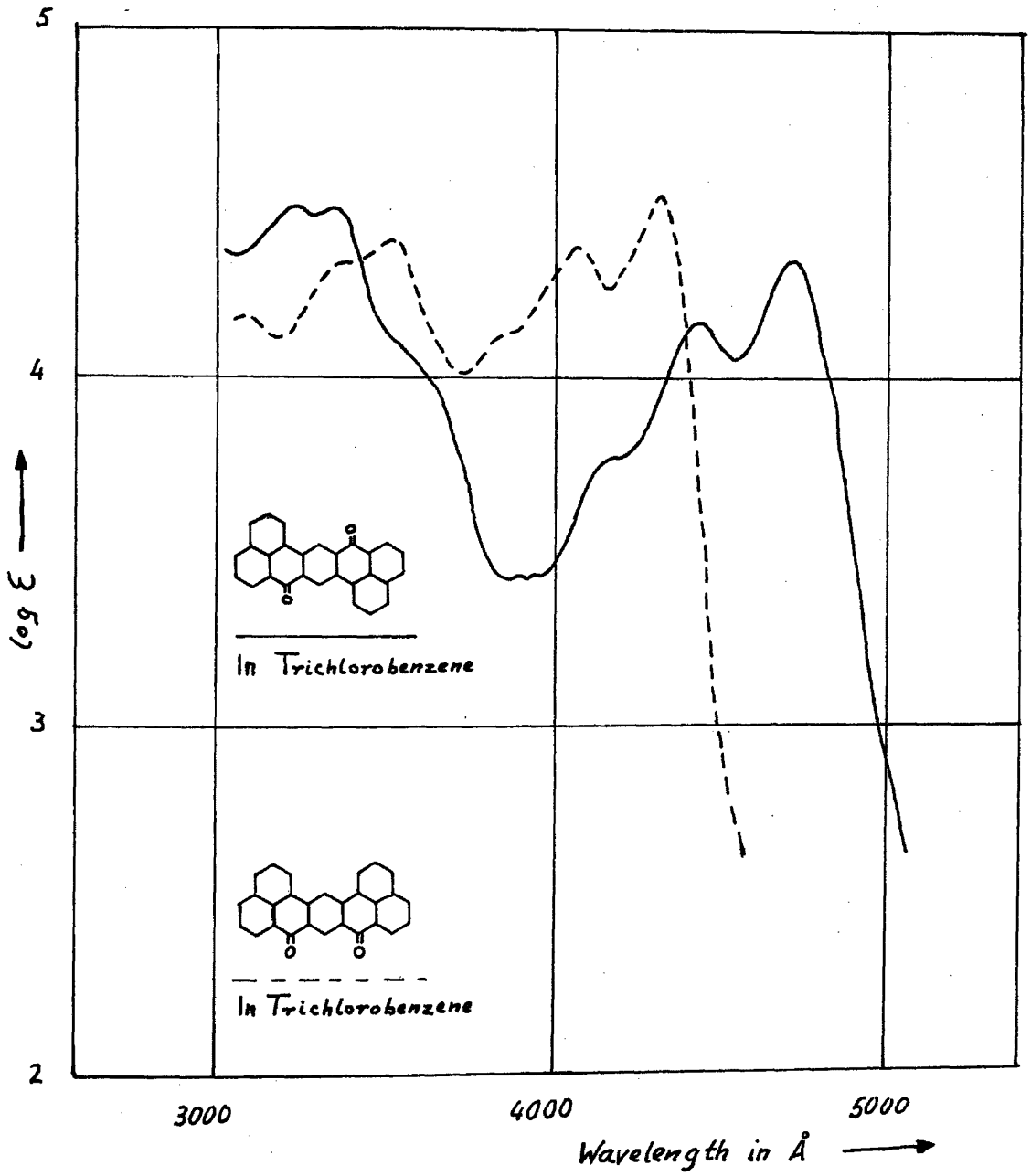

5
4
3
2
log ε
In Trichlorobenzene
In Trichlorobenzene
3000
4000
5000
Wavelength in Å

Fig. II

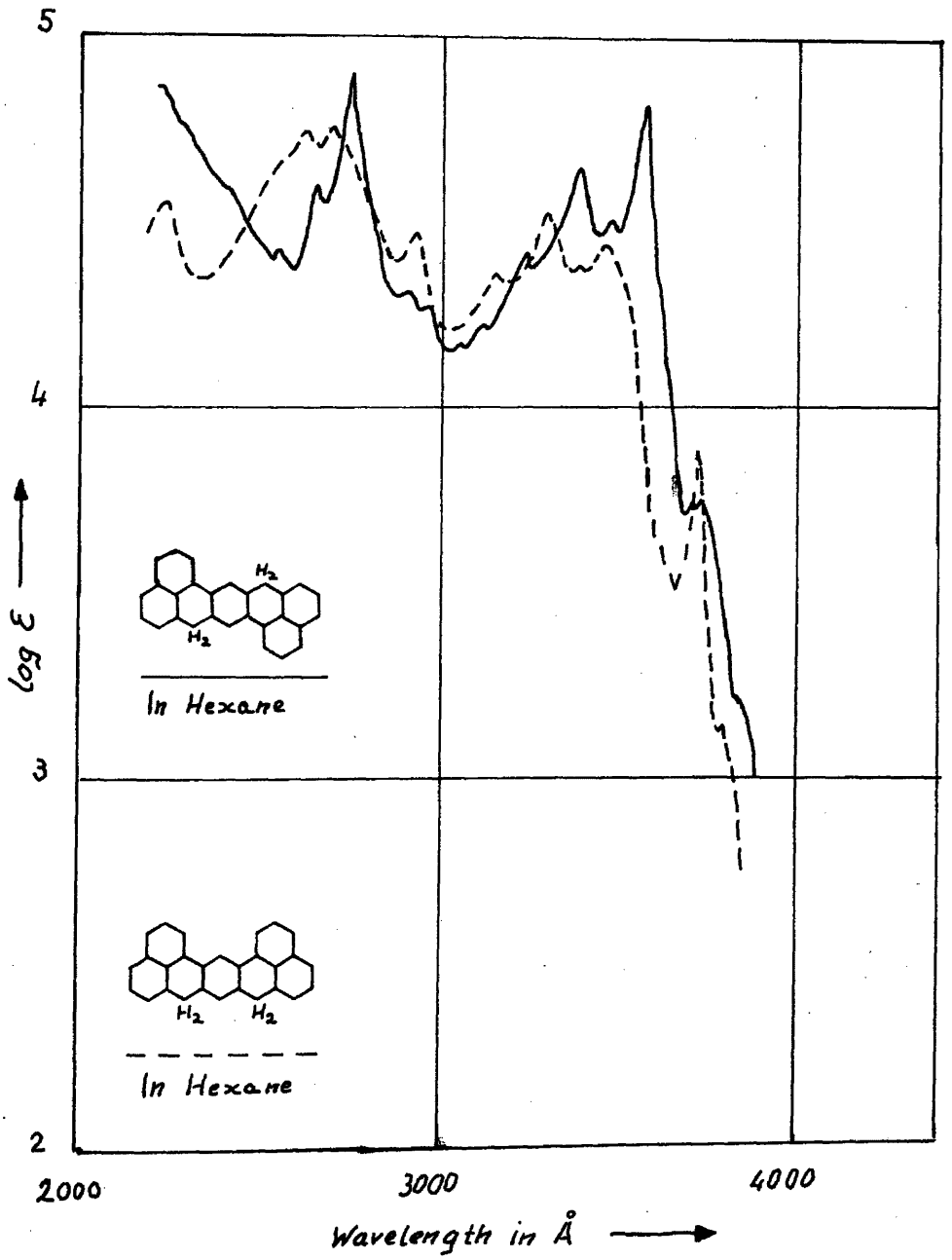

5
4
3
2
log ε
2000
3000
4000
Wavelength in Å
H2
H2
In Hexane
H2
H2
In Hexane

Fig. III

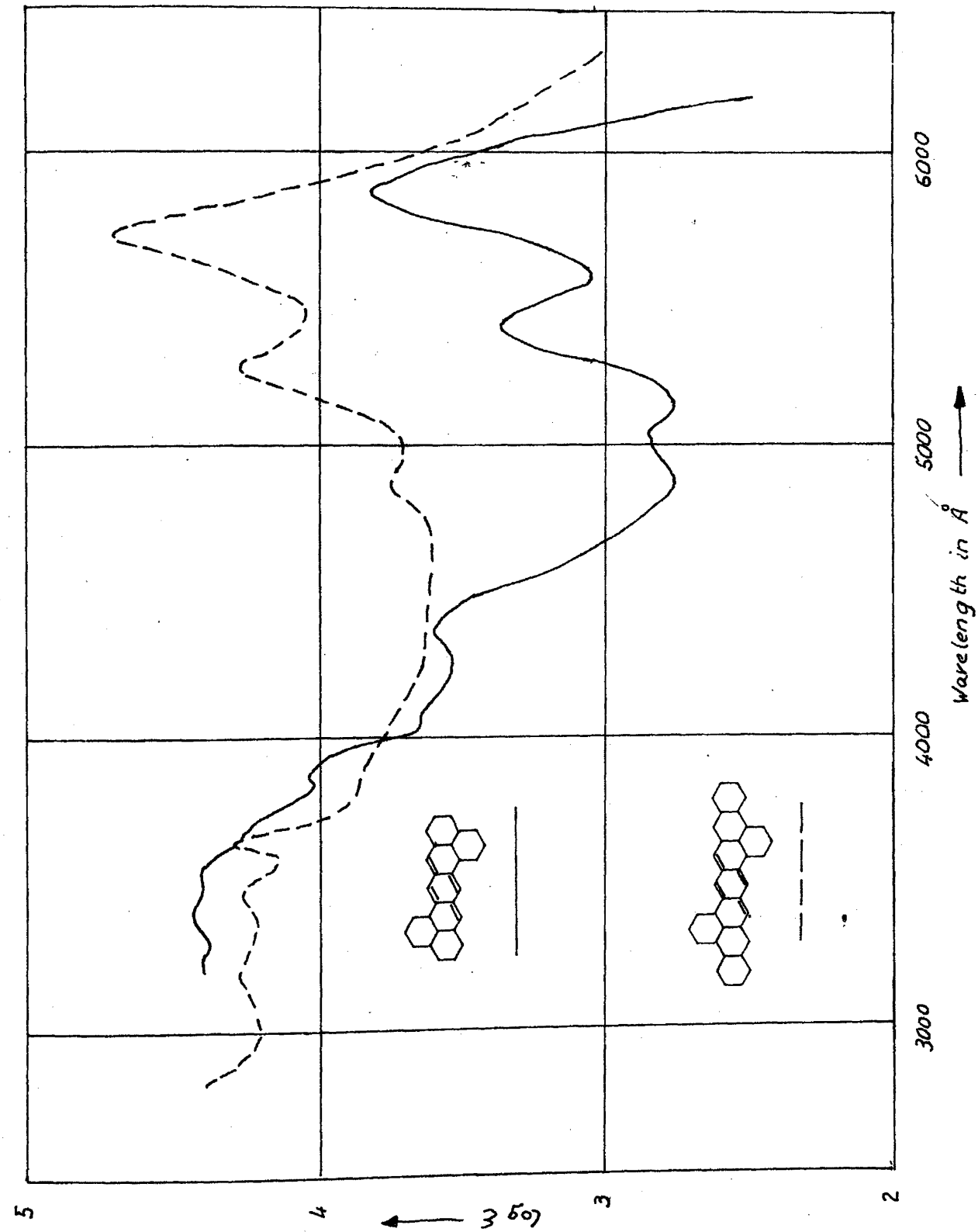
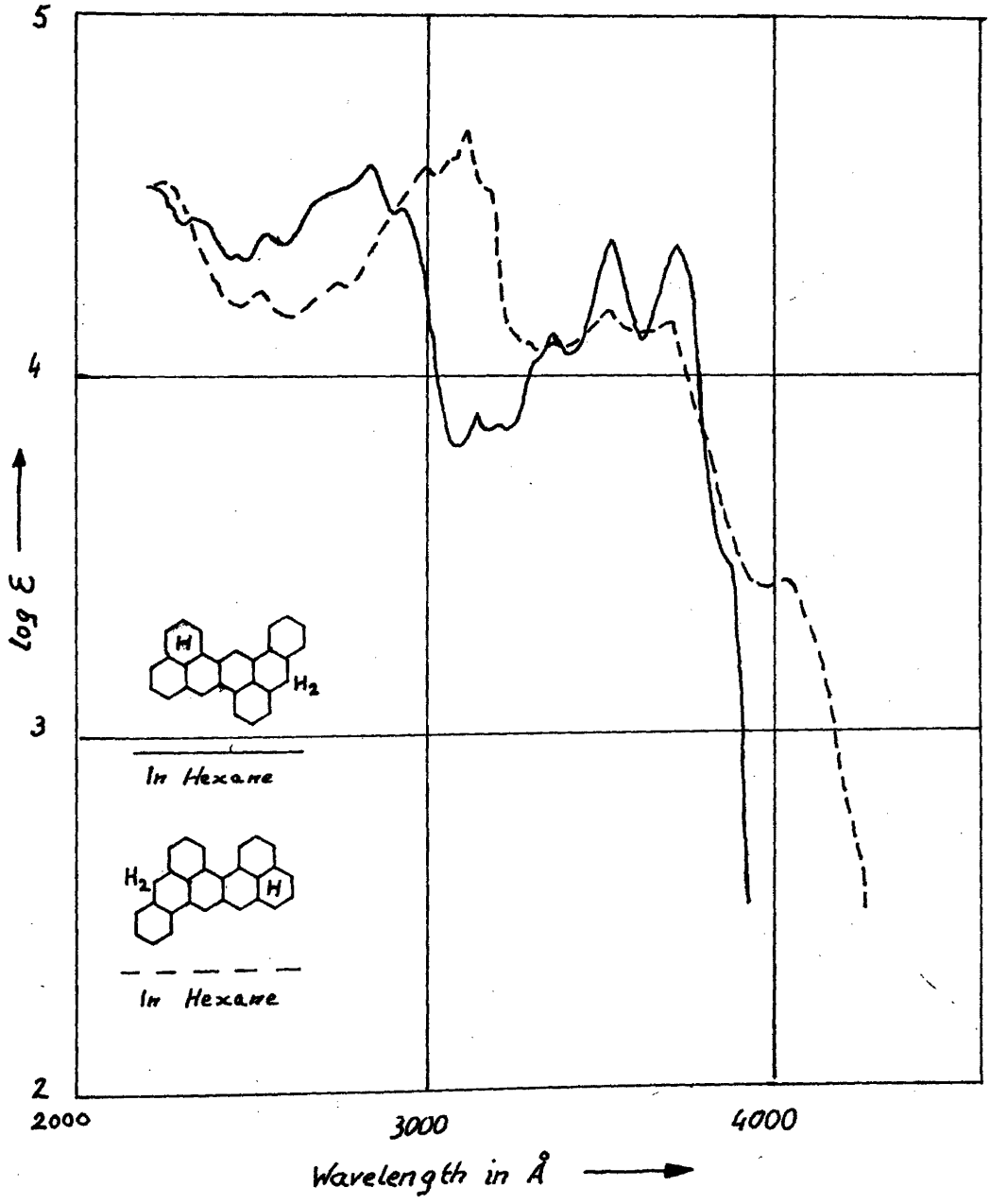
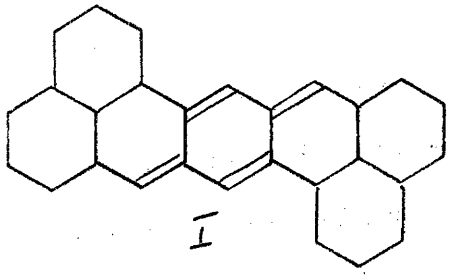


Fig. IV

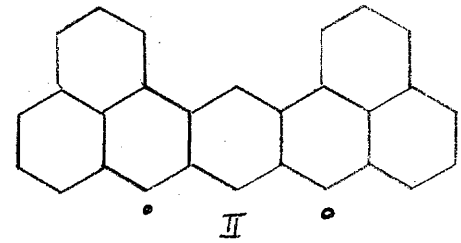

5
4
3
2
log ε
2000
3000
4000
Wavelength in Å
H
H2
In Hexane
H2
H
In Hexane

SUMMARY

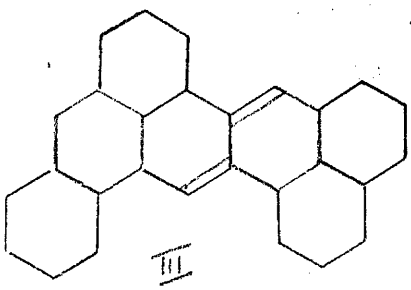
A comparative study is made of the properties and reactions of the two isomeric hydrocarbons, 7,15-dihydroheptazethrene and 1.1⁴,11.12-dibenzo-5,7-dihydropentacene. A similar investigation is carried out on hydro-derivatives of 5.6-dibenzo-zethrene and 1.2,4.5,6.7-tribenzotetracene. A chloro-derivative of 5.6,12.13-dibenzozethrene is synthesised. The behaviour of heptazethrene (I) and 5.6-benzozethrene (III) as normal aromatic hydrocarbons and the failure to observe any compound which could have the carbon skeleton of either 1.1⁴,11.12-dibenzopentacene (II) or 1.2,4.5,6.7-tribenzotetracene (IV) are explained by the latter two compounds having no Kekule structure, while the single Kekule structures of heptazethrene (I) and 5.6-benzozethrene (III) are considered sufficient to ensure normal aromatic character.



I



II



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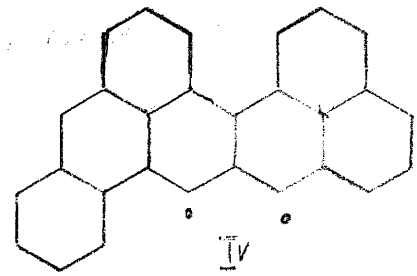
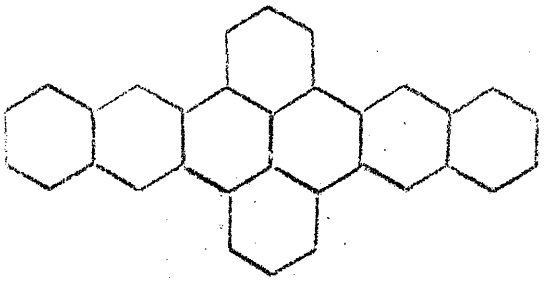
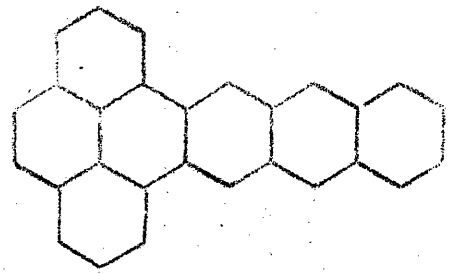


IV

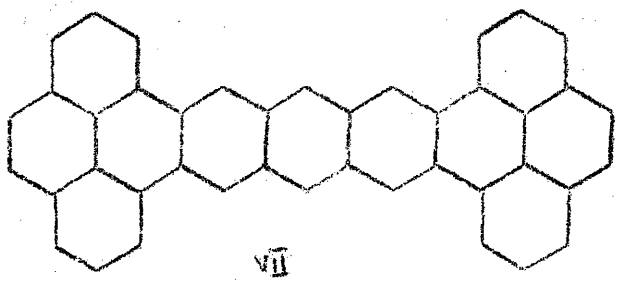
Dinaphtho-(2'.3':1.2), (2".3":6.7)-pyrene (V), anthracene-(2'.3':1.2)-pyrene (VI) and 1.14,4.5, 9.10,13.14-tetrabenzoheptacene (VII) are synthesised. The absorption spectra of these hydrocarbons are discussed with relation to other benzologues of pyrene and electronic structures are proposed for hydrocarbons of this type.



V



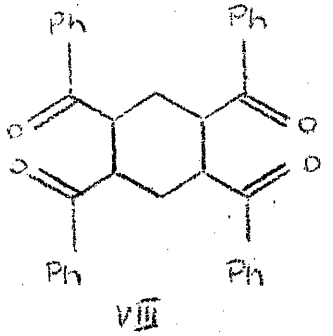
VI



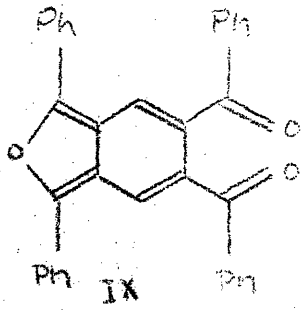
VII

The reduction of 1,2,4,5-tetrabenzoylbenzene (VIII) with copper powder in sulphuric acid is investigated with a view to the possible preparation of a compound having a bond of the Dewar type. The major product is found to be 5,6-dibenzoyl-1,3-diphenylisobenzofuran (IX). The azine derivative of this diketone (X) is found to be closely related

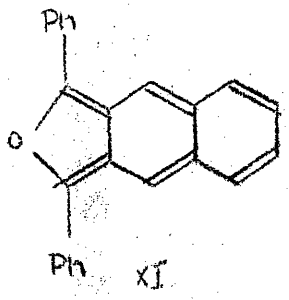
to 1,3-diphenyl-2',3'-isonaphthofuran (XI), which is obtained by reduction of 2,3-dibenzoylnaphthalene (XII). XI is the first example of a compound containing the 2,3-naphthoquinonoid system.



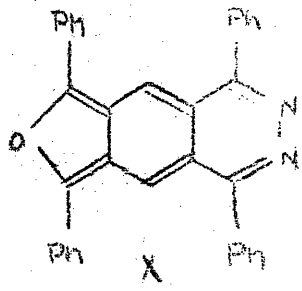
VIII



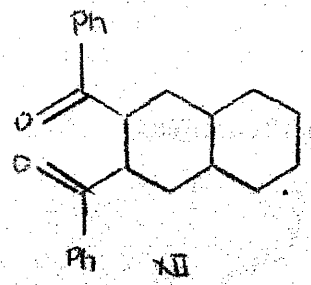
IX



XI



X



XII

Fig. V

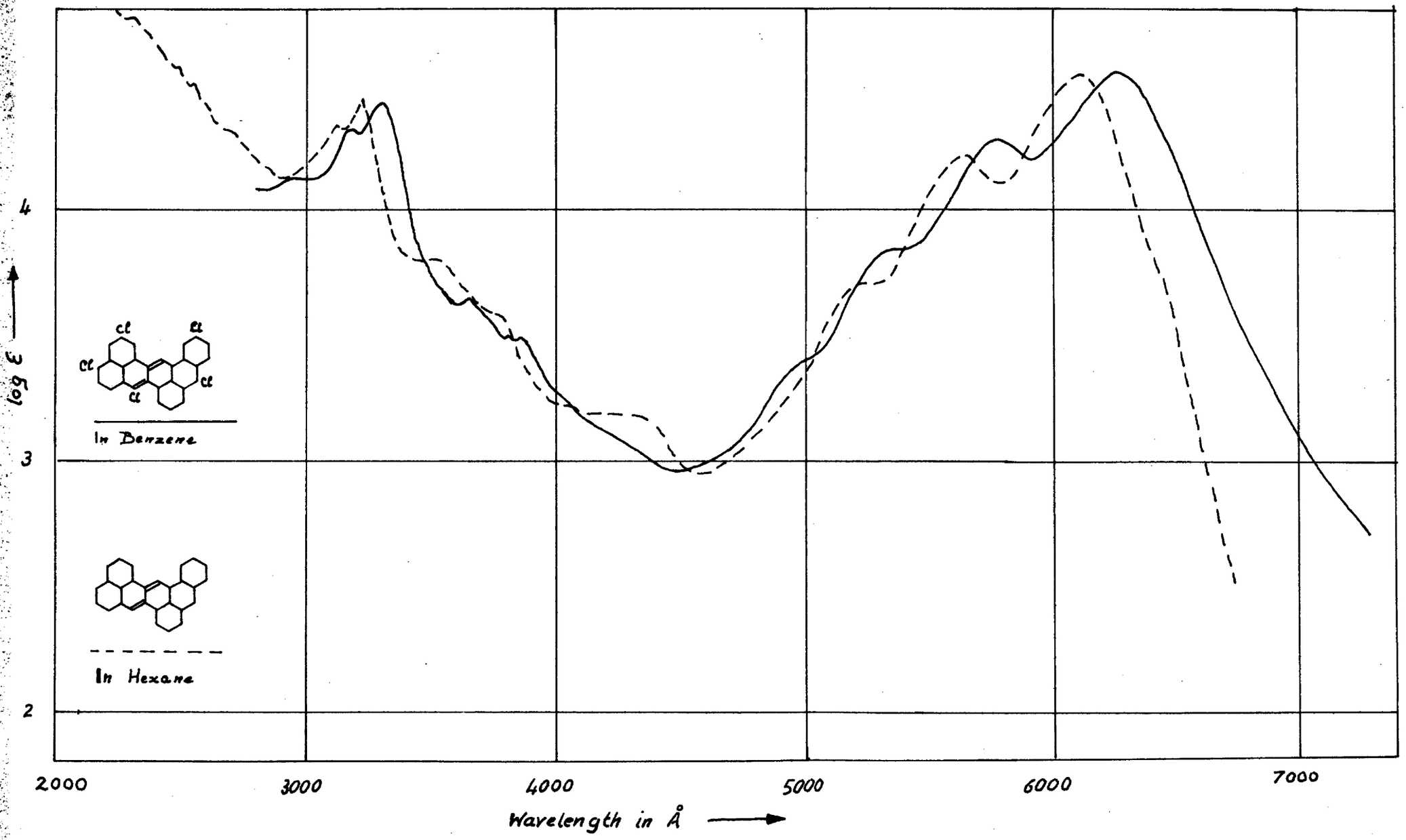
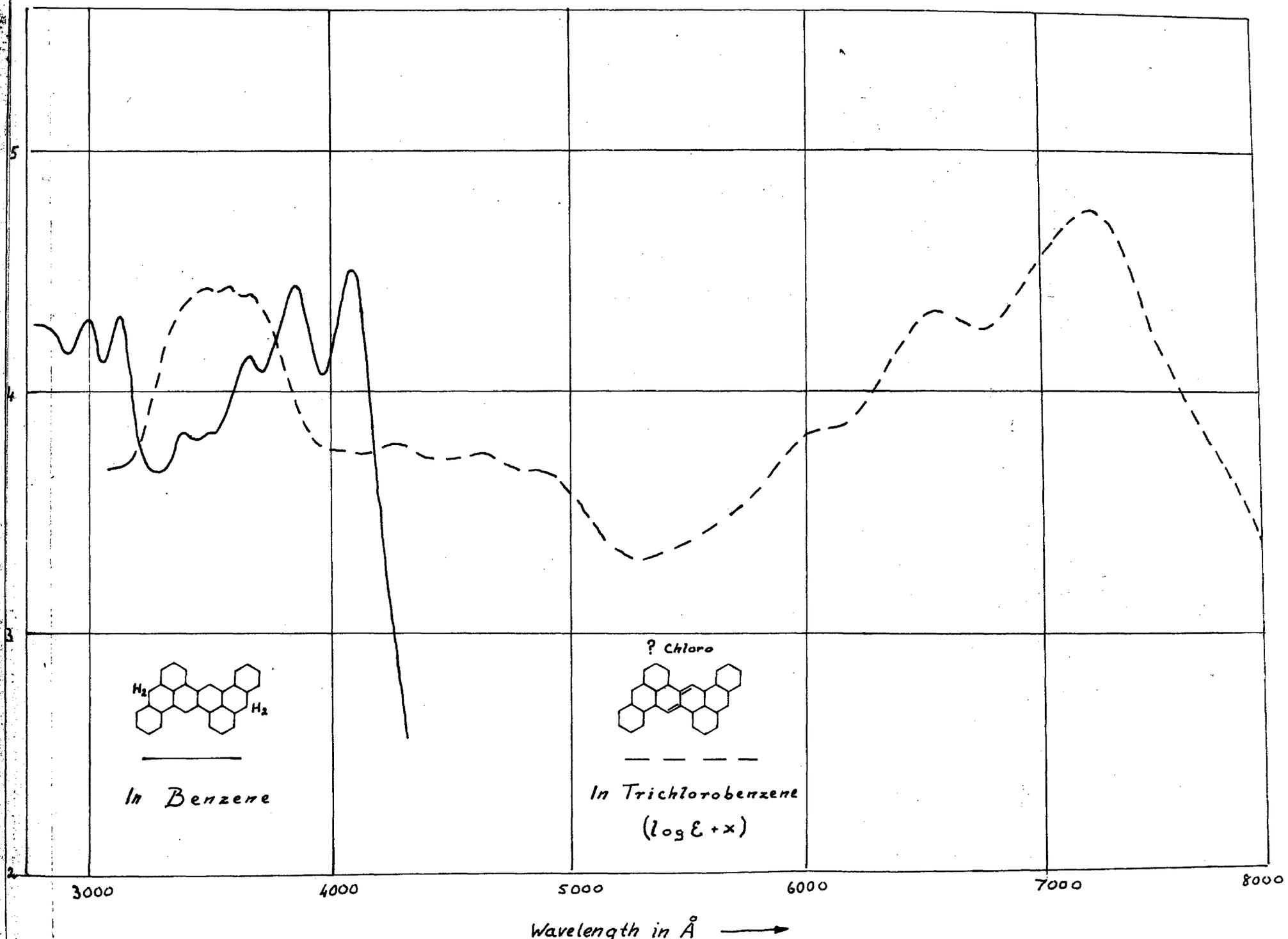

4
3
2
log ε
Cl
Cl
Cl
Cl
Cl
In Benzene
In Hexane
2000
3000
4000
5000
6000
7000
Wavelength in Å

Fig. VI


5
4
3
2
3000
4000
5000
6000
7000
8000
Wavelength in Å
? Chloro
In Benzene
In Trichlorobenzene
(log ε + x)

1,4-DI-(5,6,7,8-TETRAHYDRONAPHTHOYL) BENZENE (32) AND ELBS REACTION.

Tetralin (200 g), terephthalyl chloride (122 g) and aluminium chloride (200 g) were shaken for 3 hours at 60° in tetrachloroethane (250 ml). The complex was decomposed with dilute hydrochloric acid and the organic layer washed with dilute ammonium hydroxide. After filtration, the tetrachloroethane was distilled off leaving a brown resin which was pyrolised at 470°. Crystallisation from petrol gave colourless plates (16 g) m.p. 153°. (Found: C,93.69; H, 6.15. $C_{28}H_{22}$ requires C, 93.82; H, 6.18%. Molecular weight: 360±2 (mass spectrometer). $C_{28}H_{22}$ requires 358). No other solid material could be isolated.

REDUCTION OF 1,4-DI(α-NAPHTHOYL) BENZENE (35).

Addition of acetic acid (7 ml) to a refluxing solution of diketone (35) (1.5 g) in pyridine (15 ml) with zinc dust (3 g) gave a transient orange colour. After 20 minutes the pyridine liquors were poured into cold water and the product sublimed at 370° and 10^{-1}mm. Crystallisation from benzene/petrol gave colourless plates, m.p. 244° which dissolved in concentrated

sulphuric acid to give a red colour. (Found: C,87.44; H,4.86. $C_{28}H_{18}O_2$ requires C,87.03; H,4.72%.)

ALUMINIUM CHLORIDE MELT ON 1,4-DI(α-NAPHTHOYL)-BENZENE.

1,4-Di(α-naphthoyl) benzene (2 g), zinc dust (5 g), aluminium chloride (25 g) and sodium chloride (5 g) were stirred together at 150° for 5 minutes. After decomposition with dilute hydrochloric acid and chromatography on aluminium with xylene, the product crystallised from benzene/petrol in colourless flakes, identical with the product from the previous reaction.

1,4-DICHLORO-2,5-(α-NAPHTHOYL) BENZENE (38).

Aluminium chloride (35 g) was shaken with a solution of 2,5-dichloroterephthalyl chloride (28 g) and naphthalene (30 g) in methylene dichloride (250 ml) for 20 hours forming a deep red complex. Decomposition with dilute hydrochloric acid and extraction with dilute sodium hydroxide, hot water and ether left the diketone (38) (32 g, 88%). It crystallised from xylene in short colourless needles, m.p. 269.5°, which gave a red solution in concentrated sulphuric acid. (Found: C,74.09; H,3.61; Cl,15.30. $C_{28}H_{16}O_2Cl_2$ requires C,73.86; H,3.54; Cl,15.36%.)

HEPTAZETHRENE-7,15-QUINONE (34).

Potassium hydroxide pellets (2.5 g) were added singly to a gently boiling solution of diketone (38) (10 g) in quinoline (45 ml). After 3 hours, the solution was poured into dilute hydrochloric acid and the tar fromed extracted with hot water and dilute ammonium hydroxide. Treatment with ether left a brown powder from which heptazethrenequinone (0.8 g, 10%) was obtained. It crystallised from nitrobenzene or trichlorobenzene in orange yellow needles, m.p. 456°, and dissolved green in concentrated sulphuric acid. Alkaline sodium dithionite gave a blue vat, more easily soluble in ethanol. (Found: C,87.48; H,3.64. $C_{28}H_{14}O_2$ requires C,87.94; H,3.69%.) Yields varied from 1-10% under apparently identical conditions.

HEPTAZETHRENE-7,15-QUINONE (34).

Diketone (38) (7 g) was heated to 200° with powdered barium hydroxide (25 g). Heptazethrene-quinone (0.5 g, 9%) was sublimed from the mixture along with some unreacted diketone. The yield could not be controlled and varied from 0-9%. Cyclisation was also effected with sodium or potassium carbonate in place of barium hydroxide.

HEPTAZETHRENE-7,15-QUINONE (34).

Treatment of diketone (38) with basic copper carbonate and quinoline at 330° for 23 hours in a Carius tube yielded only traces of heptazethrene-quinone.

HEPTAZETHRENE-7,15-QUINONE (34).

Fusion of diketone (38) with potassium hydroxide in methanol at 140° gave an acid which could not be cyclised to heptazethrenequinone.

7,15-DIHYDROHEPTAZETHRENE (44).

Heptazethrenequinone (3 g) was refluxed with zinc dust (22 g) in pyridine (50 ml) and acetic acid (95%, 60 ml) added over a period of 5 hours. A transient green colour was formed at the first addition. Precipitation with dilute acetic acid and sublimation gave the hydrocarbon (0.7 g, 26%). It crystallised from xylene in short colourless needles, m.p. 386°, which dissolved slowly in concentrated sulphuric acid giving a colourless solution. (Found: C,94.71; H,4.96. $C_{22}H_{18}$ requires C,98.88; H,5.12%.)

7,15-DIHYDROHEPTAZETHRENE (44).

Heptazethrenequinone (2 g) was refluxed in cyclohexanol (35 ml) with aluminium cyclohexoxide solution (30 g), (aluminium (9 g) in cyclohexanol (100 g)) for 44 hours. Cyclohexanol and cyclohexanone were removed by slow distillation and the semi solid residue treated with dilute sulphuric acid. Crystallisation from xylene and sublimation yielded dihydroheptazethrene (0.5 g, 28%).

PHOSPHORUS, HYDRIODIC ACID REDUCTION.

Heptazethrenequinone (3 g) and red phosphorus (5 g) were refluxed for 15 hours in hydriodic acid (35%, 30 ml) and xylene (30 ml). Filtration and sublimation of the residue gave a mixture of quinone and hydrogenated derivatives of heptazethrene. The xylene layer was separated from the filtrate and washed with ammonium hydroxide. It contained a mixture of compounds giving, on dehydrogenation, solutions having the spectrum of heptazethrene. No pure hydrocarbon was obtained.

ZINC DUST MELT.

Heptazethrenequinone (0.5 g), zinc chloride (3 g), sodium chloride (0.5 g), zinc dust (0.5 g) and water (1 drop) were heated to 300°. The mixture became deep red and a sample dissolved in xylene had the spectrum of heptazethrene. The red colour quickly became brown and the reaction was stopped. Extraction with hot water left a brown resin which could not be crystallised. On treatment with dehydrogenating agents, however, it readily gave solutions having the spectrum of heptazethrene.

REACTION OF HEPTAZETHRENEQUINONE WITH ZINC DUST AND ACETIC ANHYDRIDE.

Heptazethrenequinone could not be reduced to the diacetoxy derivative of heptazethrene by treatment with zinc dust and acetic anhydride, even in the presence of a trace of iodine.

DEHYDROGENATION OF (44) WITH PALLADIUM CHARCOAL.

Dihydroheptazethrene was sublimed on to 15% palladium charcoal[16] at 300° and 10^{-2}mm. Dark green material was observed close to the palladium charcoal, but on further sublimation only light brown dihydro-heptazethrene was obtained.

DEHYDROGENATION OF (44) WITH PALLADIUM CHARCOAL.

Dihydroheptazethrene was heated with 15% palladium charcoal in trichlorobenzene in an evacuated ampule. A blood red solution was formed immediately having the spectrum of heptazethrene.

DEHYDROGENATION OF (44) WITH CHLORANIL.

Warming a solution of dihydroheptazethrene in xylene with chloranil gave immediately a deep red solution. After boiling for 3 minutes a dark green precipitate was formed. This material dissolved in benzene giving solutions having the spectrum of heptazethrene but, on sublimation, yielded only dihydroheptazethrene. If excess chloranil were used, the spectrum of heptazethrene was quickly destroyed.

DEHYDROGENATION WITH NITROBENZENE.

On heating to 160-180° a solution of dihydroheptazethrene in nitrobenzene became deep red. Samples had the spectrum of heptazethrene. If this temperature were maintained for more than 2 minutes, or if the solution were heated to boiling, oxidation occurred giving heptazethrenequinone.

REACTION OF (44) WITH MALEIC ANHYDRIDE.

Dihydroheptazethrene dissolved in molten maleic anhydride giving a deep red solution. Addition of water gave a brown precipitate which dissolved in warm dilute potassium hydroxide giving a purple solution having absorption bands at 5160, 5570 and 5970 Å.

REACTION OF (44) WITH BROMINE.

Treatment of a solution of dihydroheptazethrene in xylene with bromine gave a dark brown precipitate which became deep green on heating.

REACTION OF (44) WITH PHOSPHORUS PENTACHLORIDE.

Treatment of a solution of dihydroheptazethrene in xylene with an excess of phosphorus pentachloride gave a brown solution which became green on removal of the unreacted phosphorus pentachloride by distillation. Concentration gave a green precipitate having absorption bands at 6260 and 5740 Å in benzene.

When insufficient phosphorus pentachloride was used, the solution first became deep red (heptazethrene) and then quickly changed to blue (bands at 6000 and 5640 Å.)

REACTION OF HEPTAZETHRENEQUINONE WITH PHOSPHORUS PENTACHLORIDE.

Heptazethrenequinone (40 mg) was treated as described above with phosphorus pentachloride (1.5 g) in dichlorobenzene. The product crystallised from dichlorobenzene in blue prisms having a copper sheen which dissolved in benzene giving a bright blue solution (6220 and 5710 Å).

Powdered heptazethrenequinone (100 mg) when treated with a large excess of phenylmagnesium bromide on ether immediately formed a deep greenish blue solution, with absorption bands at 6610 and 6030 Å. No product was isolated in a pure state.

HEPTAZETHRENE HYDROCHLORIDE.

Shaking a solution of heptazethrene with concentrated hydrochloric acid produced immediately a violet precipitate. This material was insoluble in non-polar solvents and decomposed on warming or standing. It was, however, soluble in acetic acid, in the presence of hydrochloric acid, giving a violet solution (5660 and 5180 Å).

Relatively pure solutions of heptazethrene were prepared from dihydroheptazethrene by treatment

with chloranil, unreacted chloranil and its condensation products being removed with molten potassium hydroxide.

1.14,11.12-DIBENZOPENTACENE-5,7-QUINONE (40).

Potassium hydroxide pellets (2.5 g) were added gradually to a solution of 1,3-dichloro-4,6-di (α-naphthoyl) benzene (10 g) in boiling quinoline (50 ml). After refluxing for 3 hours, the solution was cooled and filtered. Extraction with ether and hot water left a brown powder (2 g). The quinoline solution was poured into an excess of dilute hydrochloric acid giving a further quantity of crude quinone (4.2 g). It crystallised from nitrobenzene in yellow needles, m.p. 435°, softening at 418-419°, which dissolved in concentrated sulphuric acid to give a violet-red solution with a red fluorescence. (Found: C,87.68; H,3.91. $C_{28}H_{14}O_2$ requires C,87.94; H,3.69%.) It gave no vat. Yields were between 20 and 29%.

1.14,11.12-DIBENZO-5,7-DIHYDROPENTACENE (43).

The quinone (40) (5 g) was refluxed with zinc dust (30 g) in pyridine (150 ml) and acetic acid (95%, 40 ml) added during 8 hours. No colouration was observed in the proximity of the zinc dust.

Precipitation with dilute acetic acid and sublimation gave the hydrocarbon (2 g, 44%). It crystallised from xylene in short colourless needles, m.p. 345°, which dissolved slowly in concentrated sulphuric acid to give a blue solution with a red fluorescence. (Found: C,94.60; H,5.18. $C_{28}H_{18}$ requires C,94.88; H,5.12%.)

DEHYDROGENATION OF (43) WITH PALLADIUM CHARCOAL.

A solution of the hydrocarbon (43) in trichlorobenzene was heated at 200° with 15% palladium charcoal[16] in an evacuated ampule for several days. No change was observed except for a gradual increase in the general absorption.

REACTION OF (43) WITH MALEIC ANHYDRIDE.

A solution of the hydrocarbon (43) in maleic anhydride was refluxed for 8 hours under carbon dioxide. After cooling, the maleic anhydride was extracted with hot water leaving a dark green tar which was completely insoluble in dilute aqueous potassium hydroxide.

REACTION OF (43) WITH PHOSPHORUS PENTACHLORIDE.

Treatment of a solution of the hydrocarbon (43) in xylene with phosphorus pentachloride gave a dark green precipitate which was insoluble in trichlorobenzene.

REACTION OF (43) WITH BROMINE.

Bromine reacted immediately with (43) in xylene solution giving a dark green insoluble precipitate.

DEHYDROGENATION OF (43) WITH CHLORANIL.

Dihydrodibenzopentacene (43) (50 g) and chloranil (215 mg) were refluxed in trichlorobenzene for 10 minutes, and the dark green precipitate produced filtered off. This was insoluble in all solvents tried and did not sublime below the softening point of pyrex. (Found: C,67.04; H,2.53; Cl,16.24%.)

2-CHLORO-1-NAPHTHOL (51).

Sodium hypochlorite solution (425 ml), containing 14% active chlorine, was added during forty minutes to a solution of 1-naphthol (116 g) in sodium hydroxide (3%, 800 ml) at 0-2°. After dropwise addition of concentrated hydrochloric acid (200 ml), the solution was stirred for thirty minutes at 10°. Crude 2-chloro-1-naphthol (129 g, 92% of theory), m.p. 48-51°, was filtered and used directly for the preparation of 2-chloroperinaphthenone-1. Steam distillation gave colourless needles, m.p. 60-62°.

2-CHLOROPERINAPHTHENONE-1 (52).

Crude 2-chloro-1-naphthol (25 g) was added slowly to a well stirred mixture of sulphuric acid (72%, 150 ml), sodium nitrobenzene-m-sulphonate (22.5 g), ammonium vanadate (0.5 g) and glycerol (50 ml) at 135°. After being stirred for thirty minutes at 140° the black frothy mixture was diluted with cold water and filtered. 2-Chloroperinaphthenone (9.4 g), m.p. 151-152.5°, was extracted from both the residue and the filtrate with hot benzene.

5.6-BENZOZETHRENEQUINONE-4,14. (47).

2-Chloroperinaphthenone (20 g) and methylene anthrone[20] (20 g) were refluxed for 3½ hours in nitrobenzene (120 ml). After cooling, filtration gave a dark yellow residue (7.8 g) which crystallised from chlorobenzene (250 ml, charcoal) affording 5,6-benzozethrenequinone (1.1 g) as golden yellow plates.

Crystallisation from xylene of the tar obtained by concentration of the nitrobenzene liquors gave a 50% recovery of the 2-chloroperinaphthenone.

TETRAHYDRO-5.6-BENZOZETHRENE (53) OR (54).

Powdered 5.6-benzozethrene quinone (0.5 g) and zinc dust (4 g) were refluxed in pyridine (20 ml) and acetic acid (93%, 18 ml) added during 7 hours. Precipitation with dilute hydrochloric acid, sublimation and crystallisation from xylene gave the hydrocarbon as short brown rods (0.07 g). (Found: C,94.17; H,6.12%.) This was further purified by chromatography on grade I alumina with benzene as eluent giving short pale pink rods, m.p. 267-268°. (Found: C,93.99; H,5.84. $C_{28}H_{20}$ requires C,94.34; H,5.66%.)

5.6-BENZOZETHRENE (49).

Tetrahydro 5.6-benzozethrene (100 mg) was sublimed through palladium charcoal[16] at 310° and 10^{-3} m.m. giving a deep blue glass (8 mg) which could not be induced to crystallise and showed considerable decomposition on resublimation. (Found: C,94.10; H,5.59. $C_{28}H_{16}$ requires C,95.43; H,4.57. $C_{28}H_{20}$ requires C,94.34; H,5.66%.) This glass dissolved in concentrated sulphuric acid giving a pale blue solution.

PENTACHLORO 5.6-BENZOZETHRENE (55).

Tetrahydro 5.6-benzozethrene was treated in chlorobenzene with excess phosphorus pentachloride giving a brown solution. Unreacted phosphorus pentachloride was removed with some chlorobenzene by distillation. Pentachloro 5.6-benzozethrene crystallised from chlorobenzene in deep violet-blue prisms. (Found: Cl,33.36. $C_{28}H_{11}Cl_5$ requires Cl,33.79%.)

5.6-BENZOZETHRENE PERCHLORATE.

A concentrated solution of tetrahydro 5.6-benzozethrene (100 mg) in benzene was refluxed for

one minute with chloranil (200 mg) forming a deep greenish blue solution. Addition of a few drops of perchloric acid gave a dark green precipitate. This material showed considerable decomposition after 30 minutes.

SOLUTIONS FOR SPECTROSCOPIC MEASUREMENTS.

For spectroscopic measurements, a solution of the blue glass (tetrahydrobenzozethrene sublimed over Pd/C) in benzene was treated with perchloric acid and the green salt formed extracted quickly and thoroughly with hexane. Decomposition of this salt, under hexane, with warm dilute ammonium hydroxide gave a relatively pure solution of 5.6-benzozethrene in hexane.

TETRAHYDRO 1.2,4.5,6.7-TRIBENZOTETRACENE (56) OR (57).

Powdered 1.2,4.5,6.7-tribenzotetracene-3,11-quinone (1.5 g) was refluxed with zinc dust (7 g) in pyridine (25 ml) and acetic acid (95%, 25 ml) added during 7 hours. Precipitation with dilute acetic acid and sublimation gave the hydrocarbon. It crystallised from petrol in pale yellow needles, m.p. 187-188°. (Found: C,93.80; H,5.80. $C_{28}H_{20}$ requires C,94.34; H,5.66%.)

DEHYDROGENATION ATTEMPTS.

1. The tetrahydro compound (56 or (57) was sublimed on to 15% palladium charcoal[16] at 300° and 10^{-2} mm. No product could be sublimed from the catalyst even though the temperature was raised to above 450°.

2. A solution of the tetrahydro compound in trichlorobenzene was heated to 200° for 16 hours with 15% palladium charcoal in an evacuated ampule but no change was observed except for a gradual increase in general absorption.

4,11-DIHYDRO-5.6,12.13-DIBENZOZETHRENE (61).

Powdered 5.6,12.13-dibenzozethrene-4,11-quinone (1.9 g) was refluxed with zinc dust (7 g) in pyridine (25 ml) and acetic acid (95%, 24 ml) added during 8 hours. After cooling, the pyridine liquors were decanted into dilute hydrochloric acid giving a beige precipitate and the remaining zinc dissolved in concentrated hydrochloric acid leaving red prisms (0.58 g). The hydrocarbon sublimed in ruby red prisms, m.p. 383°, which dissolved in concentrated sulphuric acid giving a blue solution with red fluorescence. The colour of this solution was identical with that of the quinone, both solutions having an absorption band at 5950 Å. (Found: C,94.48; H,5.28. $C_{32}H_{20}$ requires C,95.01; H,4.99%.)

? - CHLORO-5.6,12.13-DIBENZOZETHRENE.

Dihydrodibenzozethrene (61) was treated with phosphorus pentachloride in xylene. Excess phosphorus pentachloride was removed with the xylene by distillation, leaving a blue solid which dissolved in benzene giving a bright blue solution with absorption bands at 5850, 6430 and 6950 Å. (Found: Cl,39.64%.)

Attempts to prepare a chlorinated derivative of dibenzozethrene by treatment of the quinone with phosphorus pentachloride in trichlorobenzene were unsuccessful.

Treatment of 4,11-dihydro-5.6,12.13-dibenzozethrene (61) with 15% palladium charcoal in trichlorobenzene in an evacuated ampule at 200° gave only a yellow solution with green fluorescence which showed absorption at 4700 Å. The quinone dissolved in hot trichlorobenzene giving a yellow solution with green fluorescence and having an absorption band at 4700 Å.

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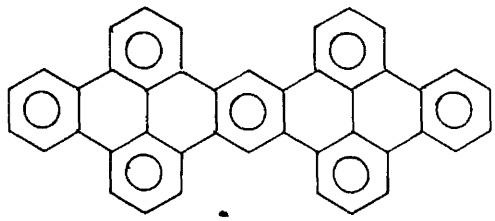
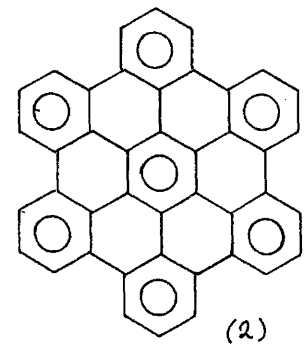
SECTION 2.

The stability of all polycyclic aromatic hydrocarbons is not a function of the physical size of the molecule as is the case in the simplest series, the acenes. In this series, the reactivity of the molecule and the wavelength of its absorption increase regularly with each linear addition of a ring. In order to explain the high stability of molecules such as tetrabenzoheptacene (1) and hexabenzocoronene (2), the theory was put forward[1] that in such hydrocarbons the electrons are not free to move throughout the whole system but are confined to the rings marked with circles (benzenoid rings).



(1)

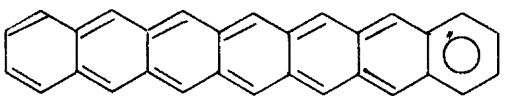


(2)

This has now been upheld by Pauncz and Cohen[2] who confirmed by molecular orbital calculations that the bond lengths of the quasi-single bonds connecting the benzenoid rings should be longer than those of

other bonds, and that the maximum free valencies are smaller than those of isomeric aromatic hydrocarbons. The known hydrocarbons which can be written, like (1) and (2), with no double bond isolated from a benzenoid ring all show the same remarkable chemical inertness, longlife phosphorescence and violet-shift of absorption spectra compared with their isomers.

The principle of writing structures with the maximum number of benzenoid rings can be applied with success to hydrocarbons other than the condensed polyphenyls. A consideration of the properties of the hydrocarbons isomeric with heptacene makes this clear[4].



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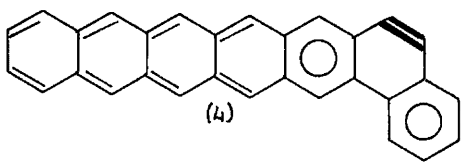
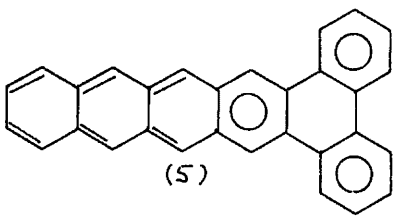


(4)



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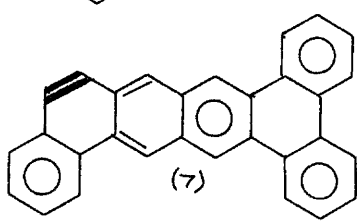

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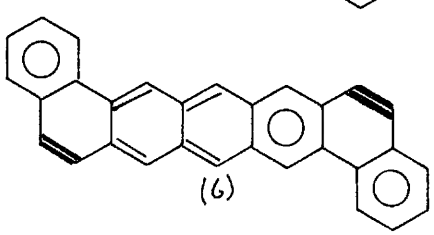

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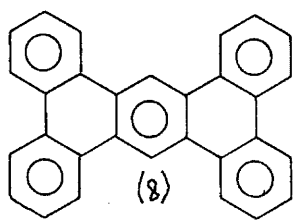


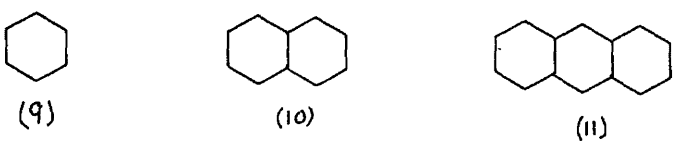
(8)

Heptacene[5] (3) is a green hydrocarbon, so reactive that it has not been obtained pure. Stability increases regularly through the series (3), (4), (5) and (6), (7) and (8) and is accompanied by a decrease in reactivity towards maleic anhydride. etc. and in the wavelength of the absorption bands. Tetrabenzotetracene[6] (8) shows the properties expected of a fully benzenoid hydrocarbon. The two isomeric dibenzopentacenes (5) and (6) each have three benzenoid rings and in agreement with this their stability, reactions and spectra are similar. Thus we have a series of six isomeric hydrocarbons whose properties vary directly with the maximum number of benzenoid rings in each.

The picture, developed by Clar[7], of a benzenoid ring containing six π electrons, four of which are confined to the ring, the remaining two, on a higher level, being capable of migration, is contrary to the molecular orbital treatment which considers all the electrons of a sextet as having mobility. It is in agreement with Hückel's[8] interpretation in-so-far as both consider the electrons to be divided between two different levels. Hückel, however, places two electrons in the lower level and four in the upper.

Using Clar's scheme it is possible to give a relatively simple explanation of the phenomena of asymmetric annellations.

If successive fusions of the same complex to opposite ends of a symmetric nucleus produce different shifts of the β-band, then this constitutes an asymmetric annellation. This is clearly shown by a comparison of the effects of annellation of a single ring and a diphenylene unit to the same nucleus (benzene).

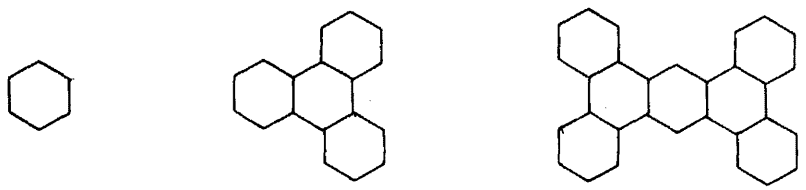


(9) (10) (11)

λ_β	1819	$\xrightarrow{391}$	2210	$\xrightarrow{305}$	2515	Å
$\sqrt{\lambda_\beta}$	42·65	$\xrightarrow{4·36}$	47·01	$\xrightarrow{3·14}$	50·15	$\sqrt{\text{Å}}$

Linear fusion of single rings to benzene ((9)-(10)-(11)) gives the well-known symmetric annellation of the acene series. Similar fusion of a diphenylene ((9)-(12)-(13)) unit gives a

large shift for the first annellation, followed by a relatively small shift for the second.



(9) (12) (13)

λ_β 1819 $\xrightarrow{751}$ 2570 $\xrightarrow{355}$ 2925 Å

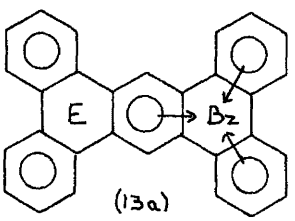
$\sqrt{\lambda_\beta}$ 42·65 $\xrightarrow{8·05}$ 50·70 $\xrightarrow{3·40}$ 54·10 $\sqrt{Å}$

50·70 − 3·40 = 47·30 $\sqrt{Å}$

$\sqrt{\lambda_\beta}$ OF NAPHTHALENE = 47·01 $\sqrt{Å}$

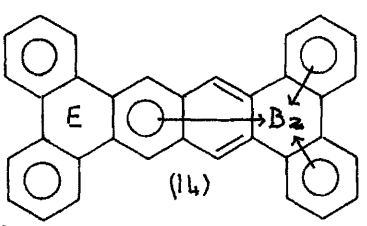
It was assumed[9] that two separate effects were operative, (a) the formation of "contact bonds" between the benzene nucleus and the diphenylene unit and (b) the conjugative effect of the additional rings. Subtraction of the second shift ((12)- (13)) from the β band of triphenylene (12) would, it was hoped, give the purely conjugative effect. In the case illustrated it can be seen that the subtraction indicated that in tetrabenzo-anthracene (13) the conjugation of the central

system was equivalent to that of naphthalene. If, using Clar's interpretation of the aromatic sextet, conjugation is caused by the migration of only two electrons from the sextet, it is clear that, at any instant, the central ring can conjugate (donate two electrons) in only one direction forming an electronically asymmetric molecule (13a).

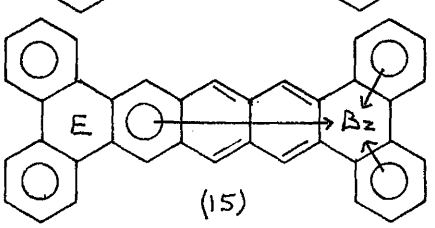


(13a)

An induced benzenoid ring (Bz) is formed at one side of the molecule by conjugation and no conjugation can take place through ring E. The same explanation holds for the higher tetrabenzacenes described so far, tetrabenzotetracene[9] (14) and tetrabenzopentacene[12] (15).

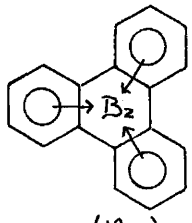


(14)

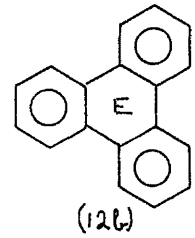


(15)

The question of whether the induced benzenoid ring (Bz) is formed in the first (Scheme I) or the second annellation (Scheme II) has been studied[12]. In the tetrabenzacene series, Scheme I would require that triphenylene should have an induced benzenoid ring (12a) and Scheme II would require an empty ring (12b).



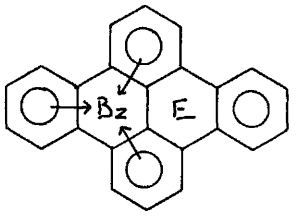
(12a)



(12b)

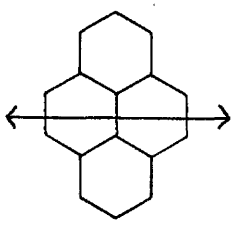
In Scheme I the total shift in the first annellation, (9) - (12), is the sum of two separate red shifts, that caused by the formation of an induced sextet, and that caused by the two newly-formed single bonds. The second shift is caused by single bond formation only. In Scheme II the first shift is attributed to the single bonds and the second shift is therefore the sum of a large red (+) shift due to the single bonds and a small violet (-) shift caused by the formation of an induced sextet. Although, at one time, Scheme II was considered in connection with Valence Bond theory, it is now thought that the original interpretation (Scheme I) is correct.

Other asymmetric annellation series so far recorded are the benzocoronenes[11], the dibenzacenes[12] and the phenylacenes[13]. In each case the ideas briefly described here have been applied and molecules, which in the molecular orbital view would be considered symmetric, are shown to be electronically asymmetric. The electronic asymmetry of dibenzopyrene (16a), mentioned by Clar[12], is considered in more detail later.

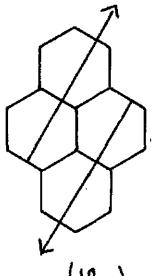


(16a)

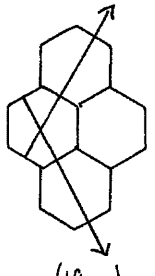
Before a complete picture of the electronic structure of pyrene can be built up an examination of the effects of the annellation of rings along each of the three electronic axes (19, x, y and z) of pyrene is necessary.



(19x)

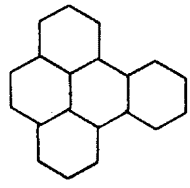


(19y)

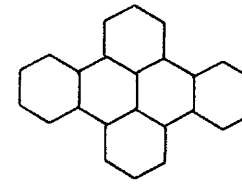


(19z)

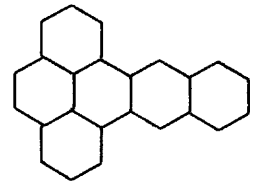
Although a considerable number of pyrenes are known annellated along axes 19y and z, until now only three hydrocarbons have been described which could be considered as being derived from pyrene by annellations along axis 19x. They are 1.2-benzopyrene (20), 1.2, 6.7-dibenzopyrene (16) and naphtho-(1.2:2'.3')-pyrene (21). The syntheses of three more hydrocarbons of this series is now described.



(20)

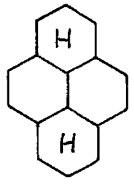


(16)

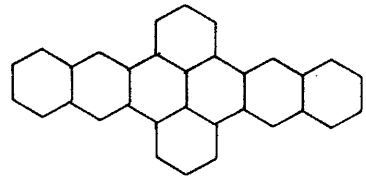


(21)

In each case the starting material was 3,4,5,8,9,10-hexahydropyrene (22) since with this compound, in contrast to pyrene itself, it is possible to carry out Friedel-Crafts condensations directly in position 1. In order to be able to complete the annellation series pyrene (19), naphthopyrene (21) and dinaphthopyrene (23), the synthesis of the latter compound was undertaken.



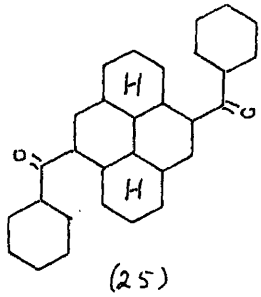
(22)



(23)

When hexahydropyrene (22) was reacted with a large excess of phthalic anhydride, in the presence of aluminium chloride, condensation occurred twice giving 1,6-di-(o-carboxybenzoyl)-3,4,5,8,9,10-hexahydropyrene (24). It is assumed that the condensation has taken place in positions 1 and 6 (and not 1 and 7) by analogy with the condensation of hexahydropyrene with benzoyl chloride from which the product was shown to be 1,6 dibenzoylhexahydropyrene[15] (25) by subsequent ringclosure to

dibenzanthanthrene[16] (26).



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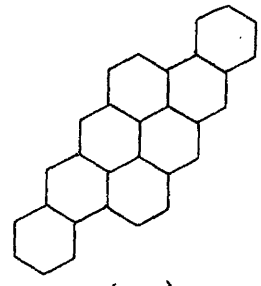
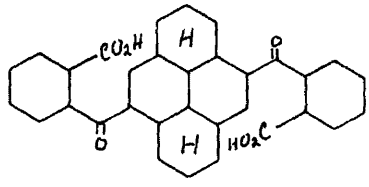


(26)

The keto-acid (24) could not be cyclised by melting with zinc chloride. It was, however, reduced in good yield to 1,6-di-(o-carboxybenzyl)-3,4,5,8,9,10-hexahydropyrene (27).



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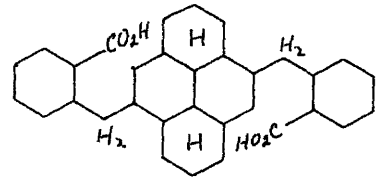
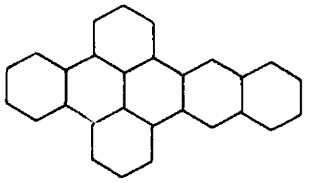
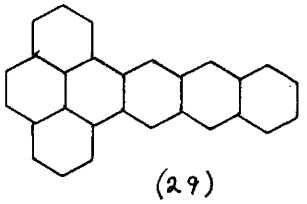


(27)

When melted with zinc chloride and sodium chloride at between 280 and 300° the dicarboxylic acid (27) was converted in high yield to dinaphthopyrene (23). This is a stable pale pink hydrocarbon whose absorption spectrum (fig. I) is closely related to that of 1.2-naphthopyrene (21) and 1.2-benzo-naphtho-(6.7:2'.3')-pyrene[17] (28).



(28)



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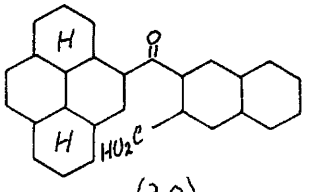
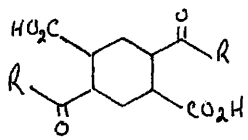


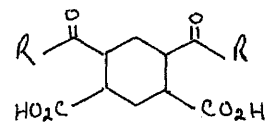
(30)

Isomeric with benzonaphthopyrene (28) is the previously undescribed anthraceno-(2'.3':1.2)-pyrene (29). Friedel-Craft's condensation of equimolar quantities of 2,3-naphthalic anhydride and hexahydropyrene (22) afforded 1-(3'-carboxy-naphthoyl-2')-hexahydropyrene (30). This reaction is analogous to the condensation of phthalic anhydride with decahydropyrene recorded by Clar[18]. Cyclisation of (30) was accomplished in a zinc chloride melt, the product consisting of a mixture of anthracenopyrene (29) and hydrogenated material. Copper powder at 300° dehydrogenated this mixture and the hydrocarbon, (29), was easily separated by sublimation. It was obtained as golden yellow plates the absorption spectrum of which is shown in fig. II.

It was found that pyromellitic dianhydride could be condensed with two molecules of hexahydropyrene (22) in the presence of aluminium chloride. The product appeared to be an inseparable mixture of the two isomers (31) and (32) (R=hexahydropyrenyl).



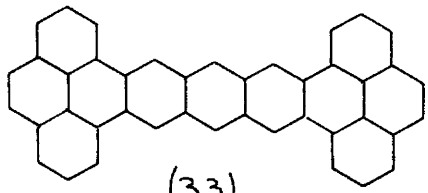
(31)



(32)

The difficulty of separation of the isomers (31) and (32) increases with the size of the hydrocarbon residue, R. Separation of the acids have been recorded when R=phenyl (C_6H_5)[19] and R=5 chloro-2-methylbenzyl (C_7H_6Cl)[20]. When, however, the hydrocarbon residue was increased to octahydrophenanthryl ($C_{14}H_{18}$)[10] no separation was effected. It was hardly surprising, therefore, that in the present case, with R increased still further, no separation could be obtained. Along with the two acids, (31) and (32), a small quantity of neutral material was produced in the Friedel-Craft's reaction. After crystallisation from xylene

this material was sublimed from copper powder giving a hydrocarbon identical with that produced by cyclisation of the acids (31) and (32) in a zinc chloride melt. 1.14,4.5,9.10,13.14- Tetrabenzoheptacene (33) is a very sparingly-soluble, high melting, deep red hydrocarbon. It was best obtained pure by sublimation at high temperature and under high vacuum. Its absorption spectrum is shown in fig. III.

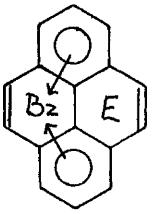


(33)

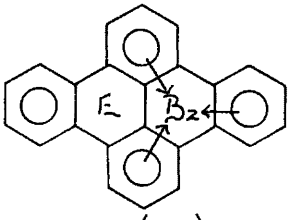
DISCUSSION.

In the following discussion an attempt is made to give an explanation of the factors involved in the determination of the wavelength of absorption of the hydrocarbons just described, (23), (27) and (33). Any such explanation must, of course, be applicable to pyrenes annellated along the other axes (19y and z).

The electronically asymmetric structure of dibenzopyrene (16a)[12] can be extrapolated to the pyrene nucleus itself (19a).

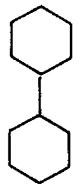


(19a)

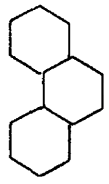


(16a)

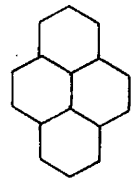
If the pyrene molecule is considered as being formed by successive fusions of a double bond to diphenyl (17), an asymmetric annellation effect is obtained in the series diphenyl (17) - phenanthrene (18) - pyrene (19).



(17)



(18)



(19)

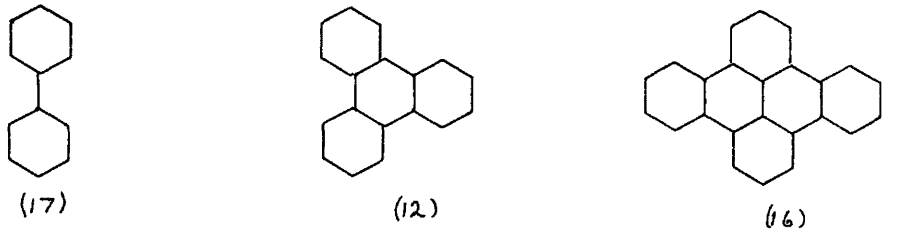
λ_β 2100 $\xrightarrow{430}$ 2530 $\xrightarrow{210}$ 2740 Å

$\sqrt{\lambda_\beta}$ 45.83 $\xrightarrow{4.47}$ 50.30 $\xrightarrow{2.05}$ 52.35 $\sqrt{Å}$

Structure (19a) is in agreement with the ability of pyrene to react with osmium tetroxide, diazoacetic ester and ozone, the attack taking place at positions 1 and 2, i.e. at the formally fixed double bond. The reactivity of pyrene in positions 3 and 8 has the same origin as the p-band absorption of pyrene. The correllation of reactivity and p-band absorption has been discussed by Clar[14]. In pyrene the p-bands are derived from positions 3 and 8 (or 10) as shown in (19b).

(19b)

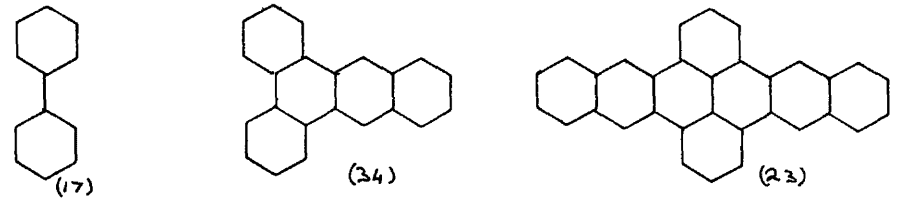
If dibenzopyrene (16) and dinaphthopyrene (23) are considered as being built up by annellations to diphenyl, asymmetric annellation effects are shown.



(17) (12) (16)

λ_β 2100 —490→ 2590 —300→ 2890 Å

$\sqrt{\lambda_\beta}$ 45.83 —5.06→ 50.89 —2.89→ 53.76 $\sqrt{\text{Å}}$



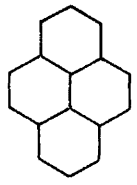
(17) (34) (23)

λ_β 2100 —800→ 2900 —210→ 3110 Å

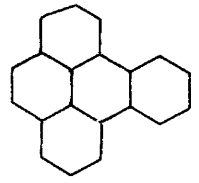
$\sqrt{\lambda_\beta}$ 45.83 —8.02→ 53.85 —1.92→ 55.77 $\sqrt{\text{Å}}$

If pyrene itself is taken as the central nucleus to which the annellations are made, asymmetric effects are still shown, this time the second

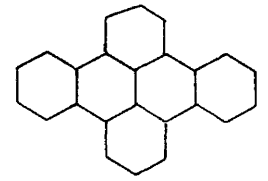
shift being negative, i.e. towards the violet.



(19)



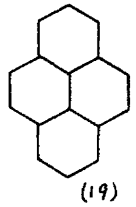
(20)



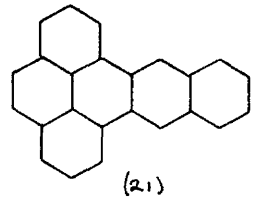
(16)

λ_β 2740 —170→ 2910 —20→ 2890 Å

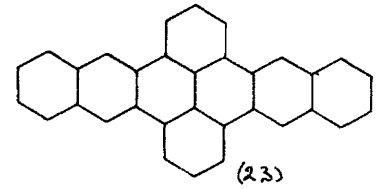
$\sqrt{\lambda_\beta}$ 52.35 —1.59→ 53.94 —0.18→ 53.76 $\sqrt{Å}$



(19)



(21)

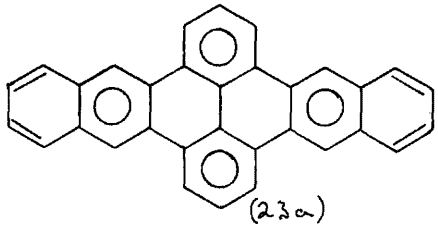


(23)

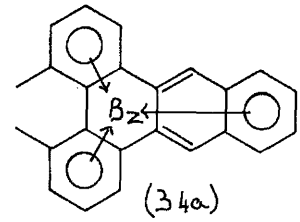
λ_β 2740 —540→ 3280 —170→ 3110 Å

$\sqrt{\lambda_\beta}$ 52.35 —4.92→ 57.27 —1.50→ 55.77 $\sqrt{Å}$

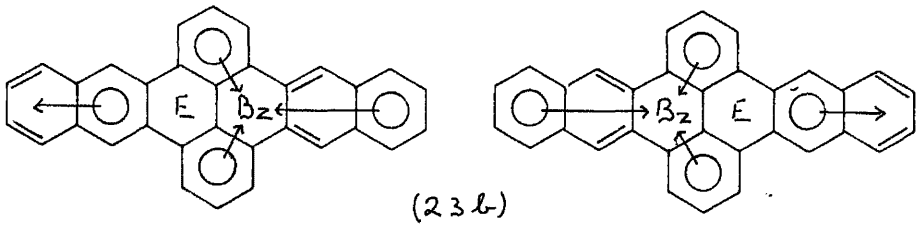
If dinaphthopyrene (23) is written with the maximum number of benzenoid rings (23a) and if the benzenoid ring is given the meaning ascribed to it by Clar[7], it can be seen, (23b), that the maximum aromatic conjugation at any instant can only be that of a substituted dibenzanthracene (34a).



(23a)



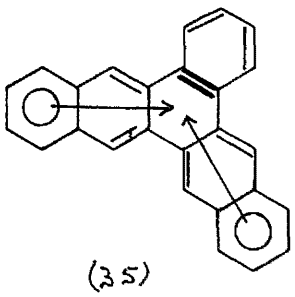
(34a)



(23b)

Since dinaphthopyrene is a symmetric molecule the rings marked "E" and Bz" can be interchanged without altering the maximum conjugation.

It has now been shown[21] that in hydrocarbons such as benzopentaphene (35) and benzoheptaphene (36) complete and simultaneous conjugation does not appear to be present in all three branches. The conjugation in the two longest branches determine the β-band, whilst conjugation in the short branch and one long branch (35a) would give rise to absorption which would be classified as β'. Benzopentaphene (35) and benzoheptaphene (36) are therefore given the instantaneous electronic conjugation shown which gives rise to the observed β-band.



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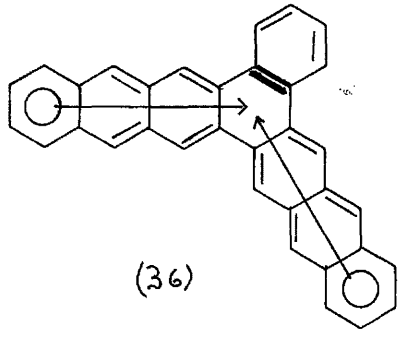
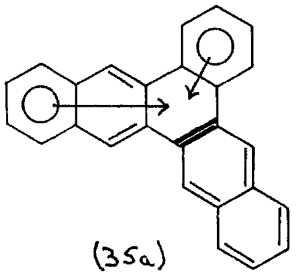
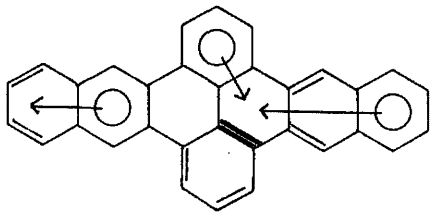


(36)



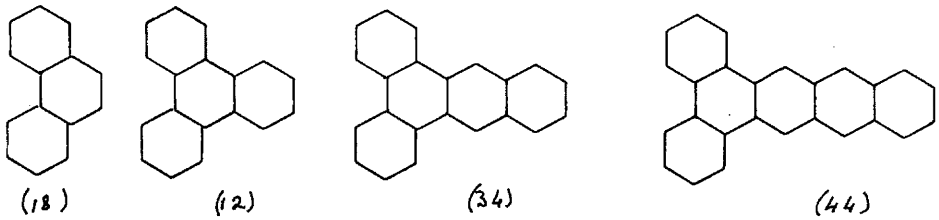
(35a)



(23c)

Thus applying Clar's interpretation of the aromatic sextet[7] the final picture of the electronic conjugation of dinaphthopyrene can be written as (23c). This accounts well for the stability of the hydrocarbon and the marked similarity of its spectrum with that of dibenzanthracene (34).

Turning now to anthracenopyrene (29) and tetrabenzoheptacene (33), the β band of the former was found to be close to the value expected by a comparison of the series phenanthrene (18) - triphenylene (12) - dibenzanthracene (34) - dibenzotetracene (44), and pyrene (19) - benzopyrene (20) - naphthopyrene (21) - anthrenopyrene (29).

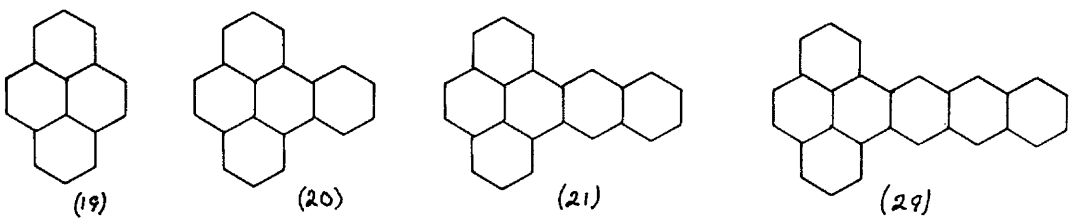


(18) (12) (34) (44)

λ_β 2530 —60→ 2590 —310→ 2900 —280→ 3180 Å

$\sqrt{\lambda_\beta}$ 50.30 —0.59→ 50.89 —2.96→ 53.85 —2.54→ 56.39 $\sqrt{Å}$

3.05 $\sqrt{Å}$ 3.42 $\sqrt{Å}$ 3.23 $\sqrt{Å}$

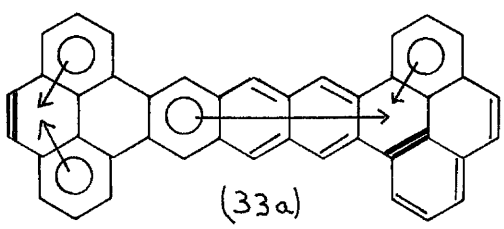


(19) (20) (21) (29)

λ_β 2740 —170→ 2910 —370→ 3280 —275→ 3555 Å

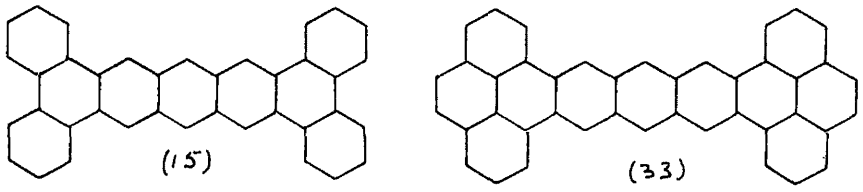
$\sqrt{\lambda_\beta}$ 52.35 —1.59→ 53.94 —3.33→ 57.27 —2.35→ 59.62 $\sqrt{Å}$

Application of the arguments used to explain the electronic asymmetry of dinaphthopyrene and the tetrabenzacenes etc.[7] to tetrabenzoheptacene (33) would require that this hydrocarbon also should be electronically asymmetric, (33a).



(33a)

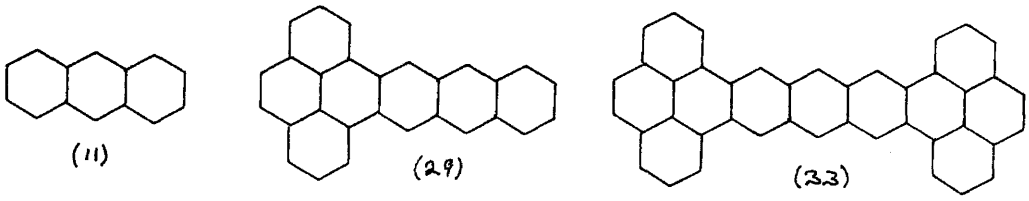
The asymmetry of tetrabenzoheptacene can be verified in two ways by an examination of observed spectral shifts. The shifts recorded for the fusion of one double bond to dibenzacenes forming the respective pyrenes (12) - (20), (34) - (21) and (44) - (29) all lie within the range $3.25 \pm 0.2 \sqrt{\text{Å}}$. Fusion of two double bonds to tetrabenzopentacene (15) forming the "double pyrene", tetrabenzoheptacene (33) results in a shift of only $2.90 \sqrt{\text{Å}}$. This is less than half the shift that would be expected if tetrabenzoheptacene were electronically symmetric.



λ_β	3480	350 →	3830	Å
$\sqrt{\lambda_\beta}$	58.99	2.90 →	61.89	$\sqrt{\text{Å}}$

Alternatively, it is clear from the shifts in the series anthracene (11), anthracenopyrene (29) and tetrabenzoheptacene (33) that these three hydrocarbons form a new asymmetric annellation

series.

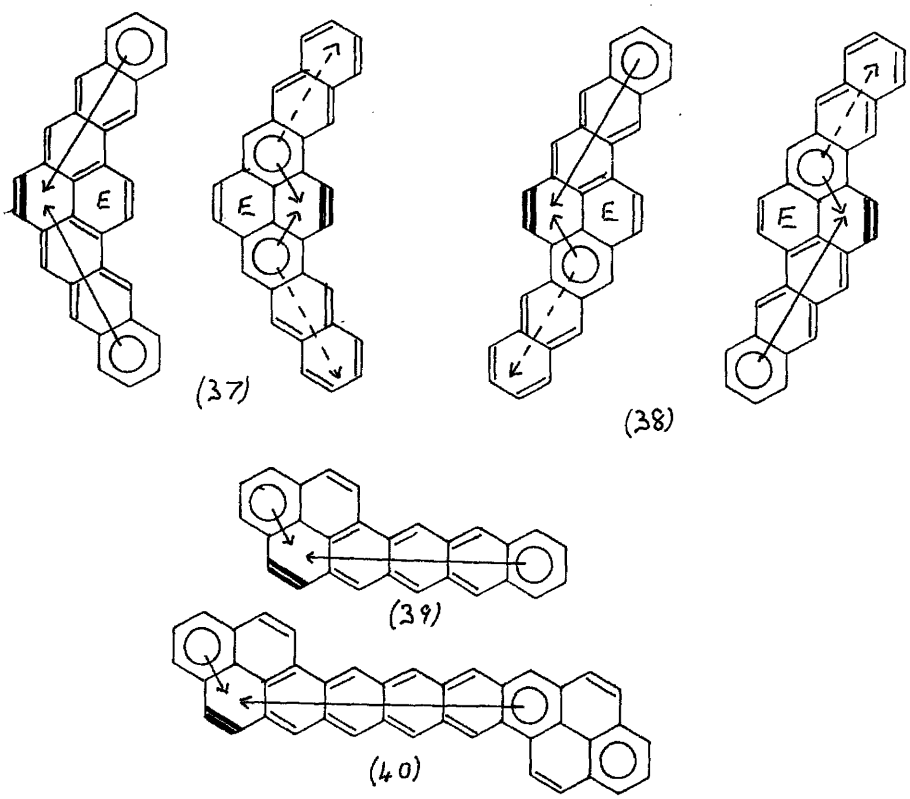


λ_β	2535	1020	3555	275	3830	Å
$\sqrt{\lambda_\beta}$	50·35	9·27	59·62	2·27	61·89	$\sqrt{Å}$

These observed spectral shifts are in agreement with tetrabenzoheptacene having the electronically asymmetric structure (33a).

As a test of the applicability of the above treatment to pyrenes annellated along axes (19y) and (19z), the spectra of dinaphthopyrene (23), anthracenopyrene (29) and tetrabenzoheptacene (33) are compared with those of the corresponding isomeric hydrocarbons (37), (38), (39) and (40) (figs. IV, V, II and III). The increased acene character of pyrenes annellated in the 3.4-positions is illustrated both by these spectral comparisons and by the picture of the conjugation in these molecules obtained by application of

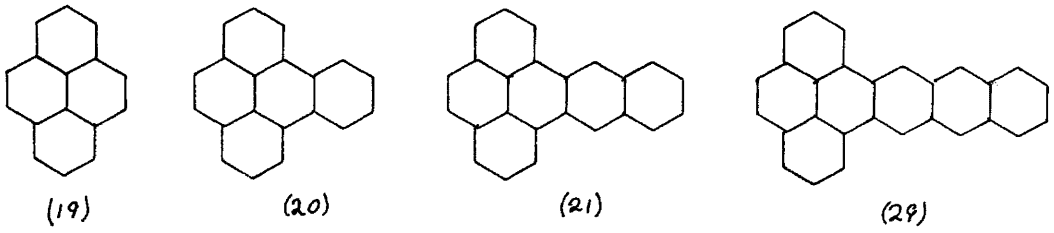
the concept of the mobile pair of π electrons.



The conjugation in dibenzopyrene (37) can occur in two dissimilar ways (as shown) while in dibenzopyrene (38) the two methods of conjugation would give rise to the same absorption. This is shown in the absorption spectra by the multiplicity of the *B*-band of dibenzopyrene (37) compared with the relatively simple *B*-band of dibenzopyrene (38).

When considering the p-band absorption in the spectrum of anthrenopyrene (29) in relation

to the series pyrene, 1.2-benzopyrene and 1.2-naphthopyrene, it must be remembered that in pyrene the p-bands are derived from positions 3 and 8 (or 10)[14].



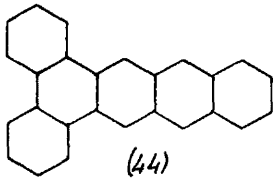
(19) (20) (21) (29)

λ_p 3335 3315 3450 ——970——→ 4420 Å

Linear extension of an acene by one ring produces an observed shift towards the red in the p-band absorption of approximately 1000 Å. The shift produced by a linear extension of the acene branch of 1.2-naphthopyrene is of this order (970 Å). Extrapolation would lead to a value of 2480 Å for the p-absorption of 1.2-benzopyrene (derived from the acene branch). This is, of course, well below the value of the p-band of the pyrene complex and would be concealed.

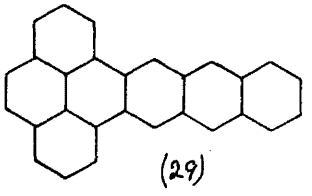
Thus, in the above series, it is considered that there are two sources of p-band absorption (and hence reactivity), that derived from the

pyrene complex and that derived from the acene branch. As the acene branch is extended its effect becomes relatively more important than that of the pyrene complex, and the p-absorption and reactivity of the molecule are determined by this. If this explanation were correct fusion of a double bond across positions 4' and 1" of dibenzotetracene (44) would be expected to have very little effect on the p-band absorption. A comparison of the p-bands of anthracenopyrene (29) and dibenzotetracene shows very little difference.



(44)

λ_p (benzene) 4415 4140 3920 3720 Å

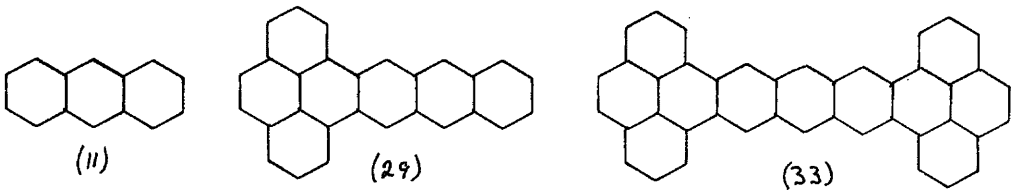


(29)

λ_p (benzene) 4420 4150 3930 3720 Å

Support is lent to the above idea by consideration of the series, anthracene, anthraceno-

pyrene, and tetrabenzoheptacene.



λ_p 3745 $\xrightarrow{675}$ 4420 $\xrightarrow{640}$ 5060 Å

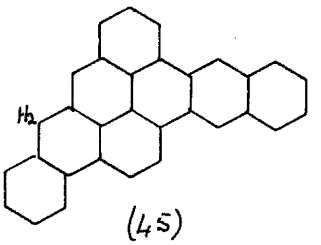
If the origin of the p-absorption of anthracenopyrene were derived from the acene branch, it would be expected that the annellation of a phenanthrene complex at one end of anthracene would have the same effect as the addition of a second similar complex at the other end. This is found to be the case.

This comparison will only be valid, however, if the p-bands originate from the same transition in each case.

APPENDIX.

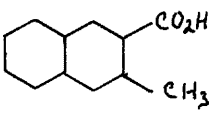
An unsuccessful attempt was made to obtain 1.2,6.7-dinaphthopyrene (23) directly by pyrolysis (in the presence of copper powder) of the product from Friedel-Craft's condensation of o-toluyl chloride with hexahydropyrene. Water and oil distilled smoothly from the reaction flask and no charring was observed even at 445°. By repeated sublimation, chromatography and crystallisation, however, only a small quantity of a yellow hydrocarbon was isolated. The absorption spectrum of this compound is very similar to that of 1.2-naphthopyrene (fig. VIII). Absorption bands were observed visually in an extract from the crude Elb's product at 5890, 5445 and 5020 Å. It seems likely that these bands were due to the presence of dibenzanthanthrene[16], methyl groups being easily split off under the conditions of the reaction. If this is the case then the yellow hydrocarbon isolated from the reaction may have structure (45). The similarity of the spectrum of this hydrocarbon with that of 1.2-naphthopyrene does not exclude

this possibility.

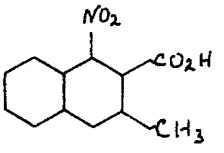


(45)

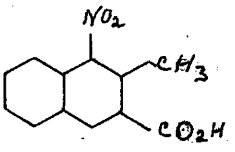
Although o-toluic acid is relatively easily prepared by oxidation of o-xylene with nitric acid[22] the preparation of 3-methyl-2-naphthoic acid (41) has been described only recently[23]. Since few experimental details were available an attempt was made to verify this report by oxidation of 2,3-dimethylnaphthalene with dilute nitric acid, using manganese dioxide as catalyst. The only acid isolated, however, would appear to be either (42) or (43).



(41)



(42)



(43)

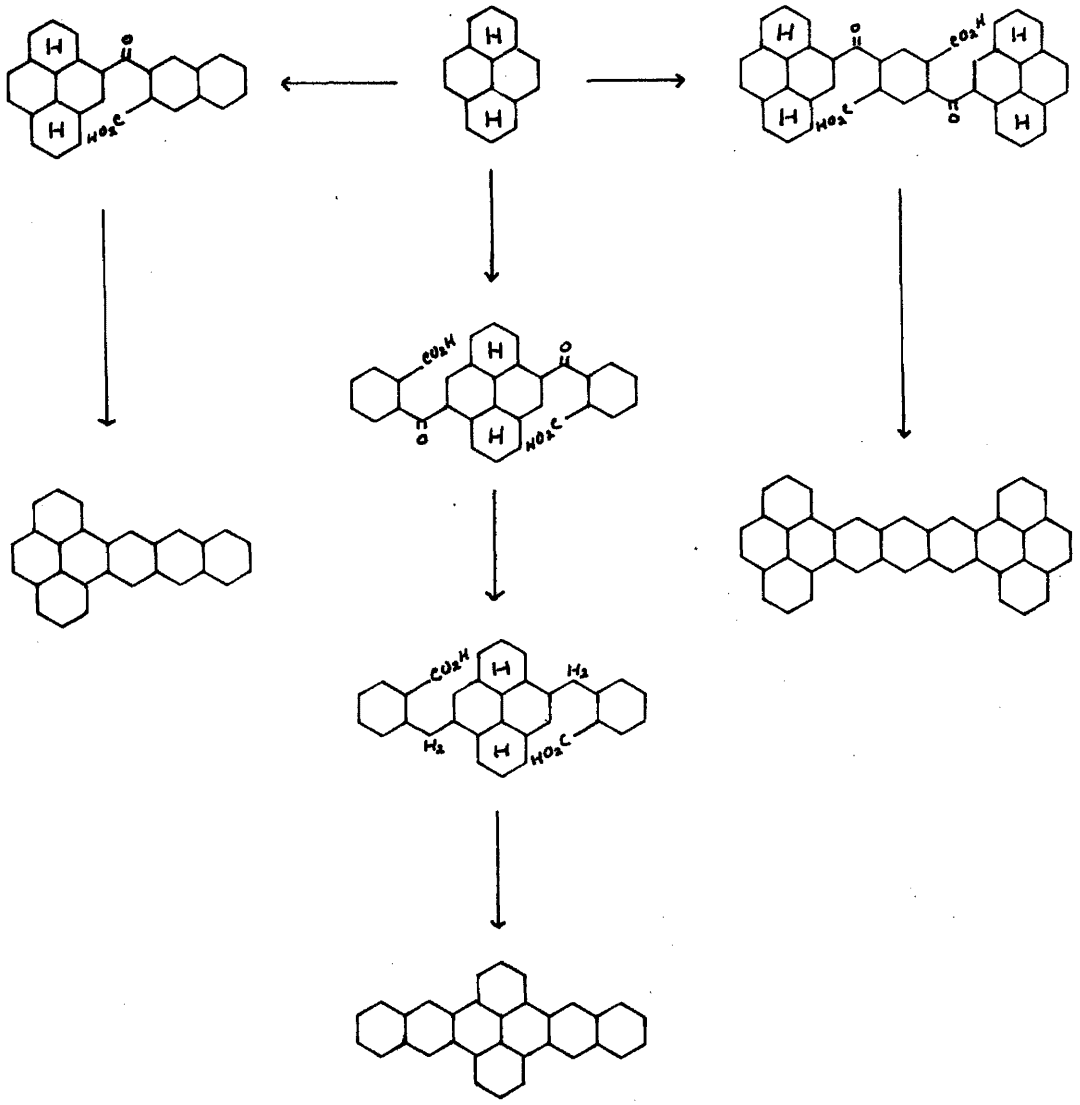

H
H
H
HO2C
O
CO2H
H
H
HO2C
O
O
CO2H
H
H
HO2C
O
O
CO2H
H
H
HO2C
H2
H2
CO2H
H
H
HO2C

Fig. I

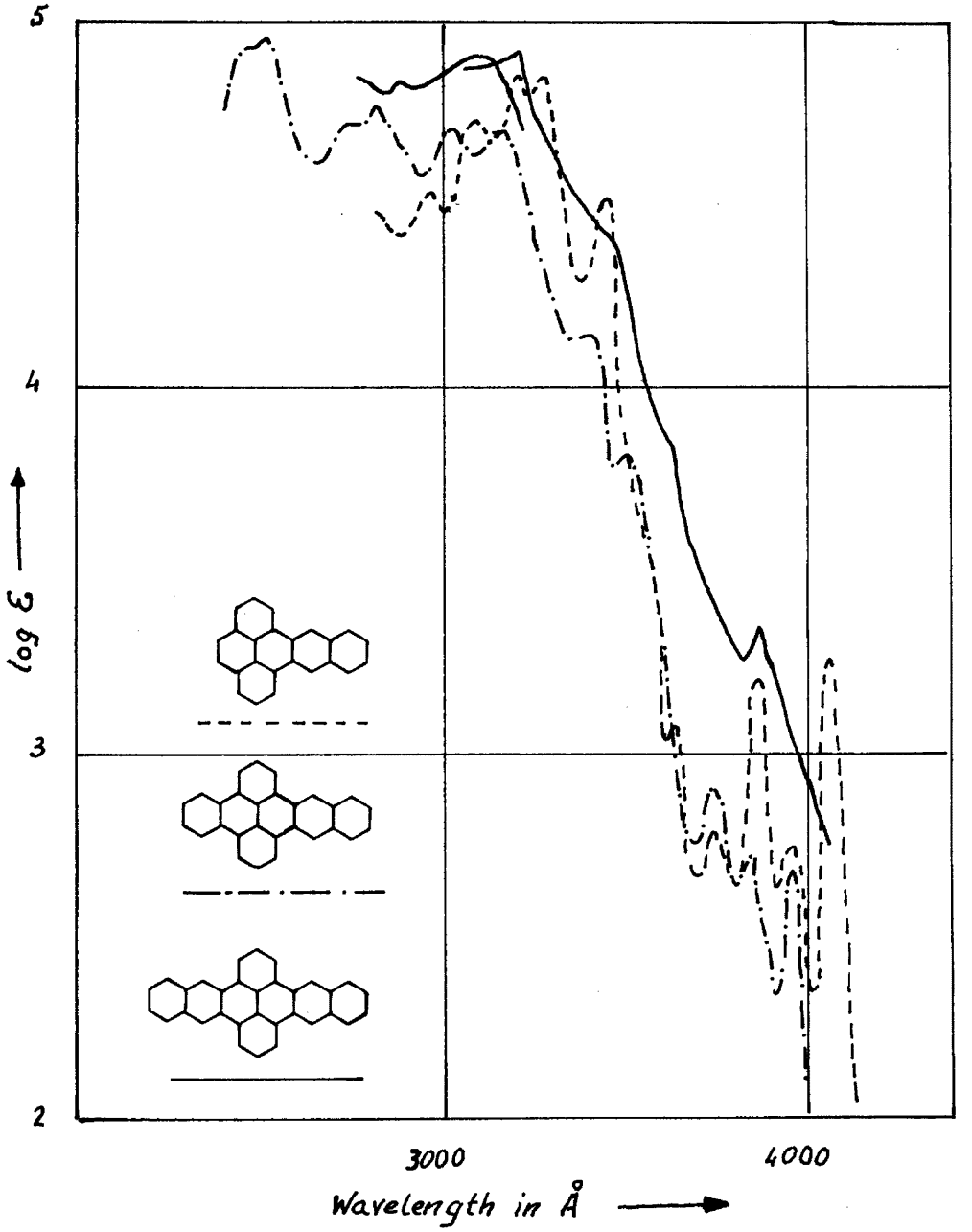


Fig. II

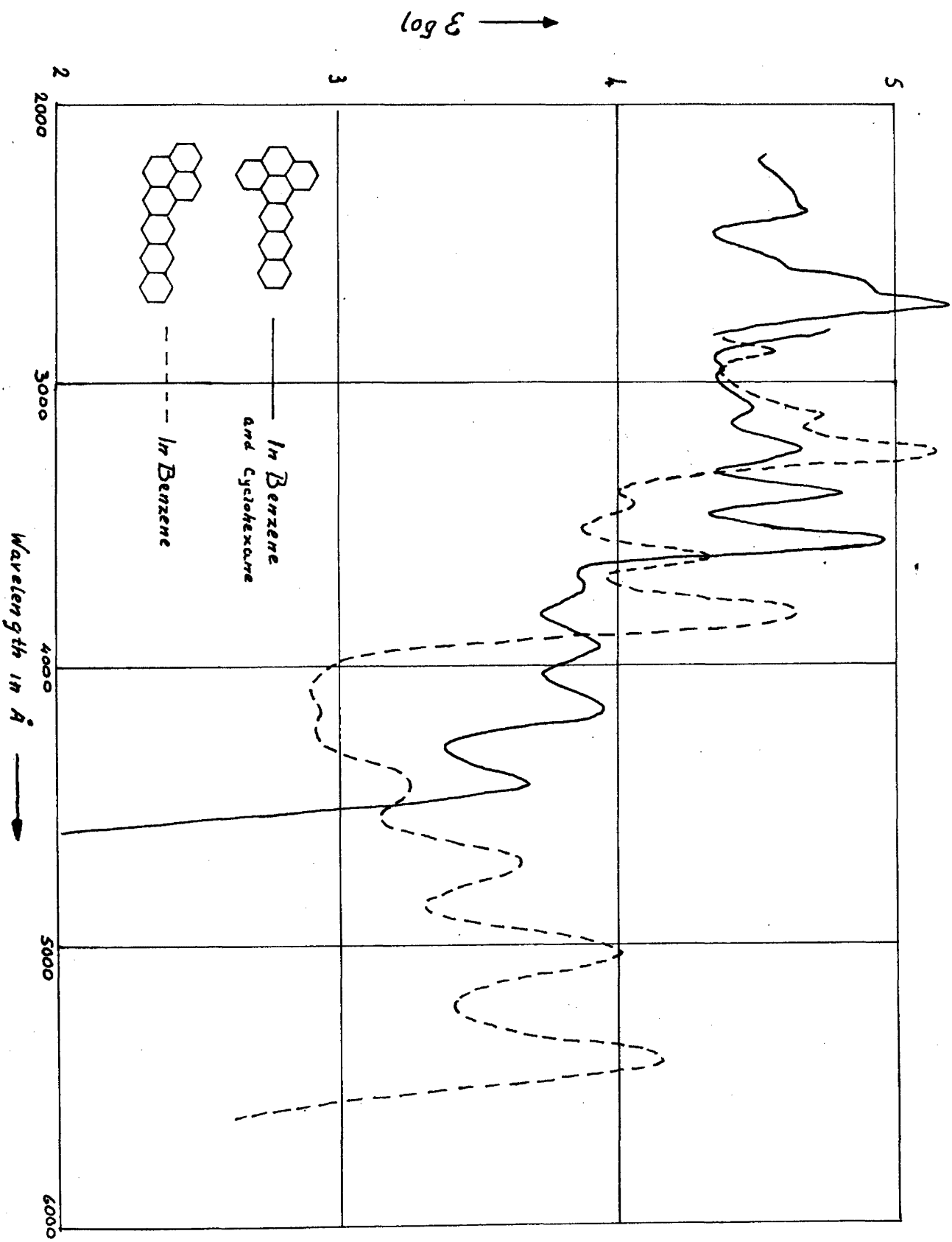

log ε
2
3
4
5
2000
3000
4000
5000
6000
Wavelength in Å
In Benzene and Cyclohexane
In Benzene

Fig. III

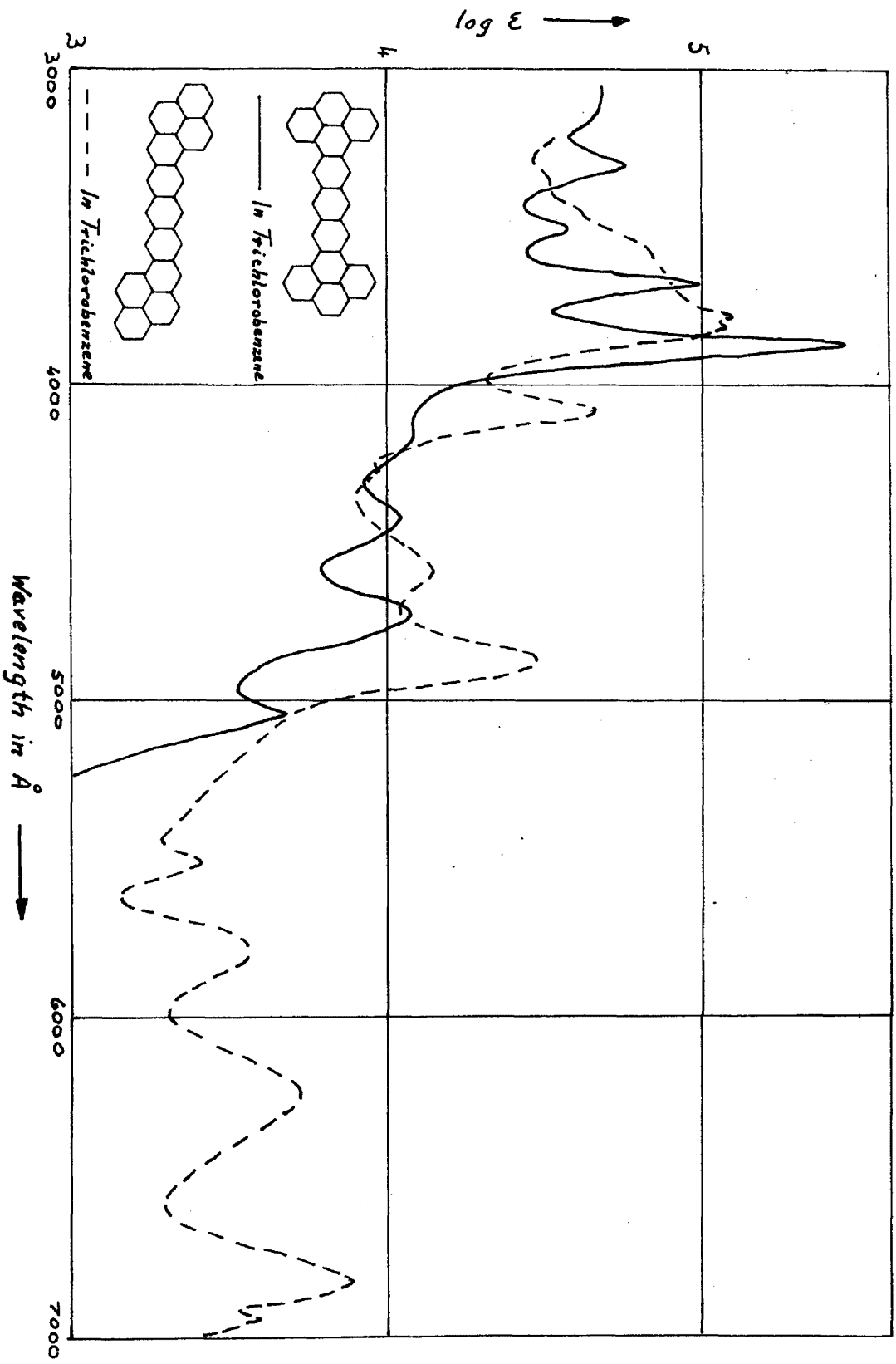

log ε
3
4
5
3000
4000
5000
6000
7000
Wavelength in Å
In Trichlorobenzene
In Trichlorobenzene

Fig. IV

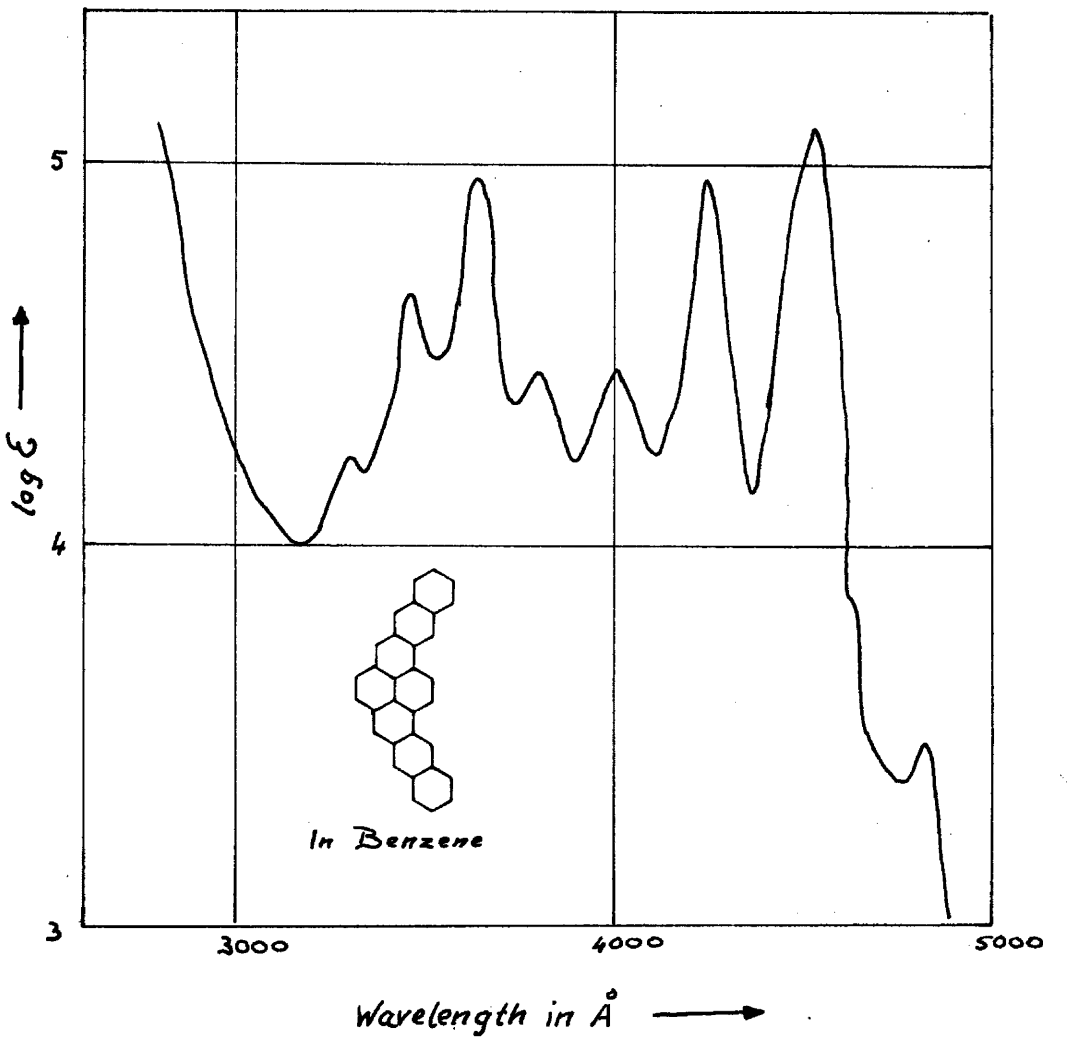


Fig. V

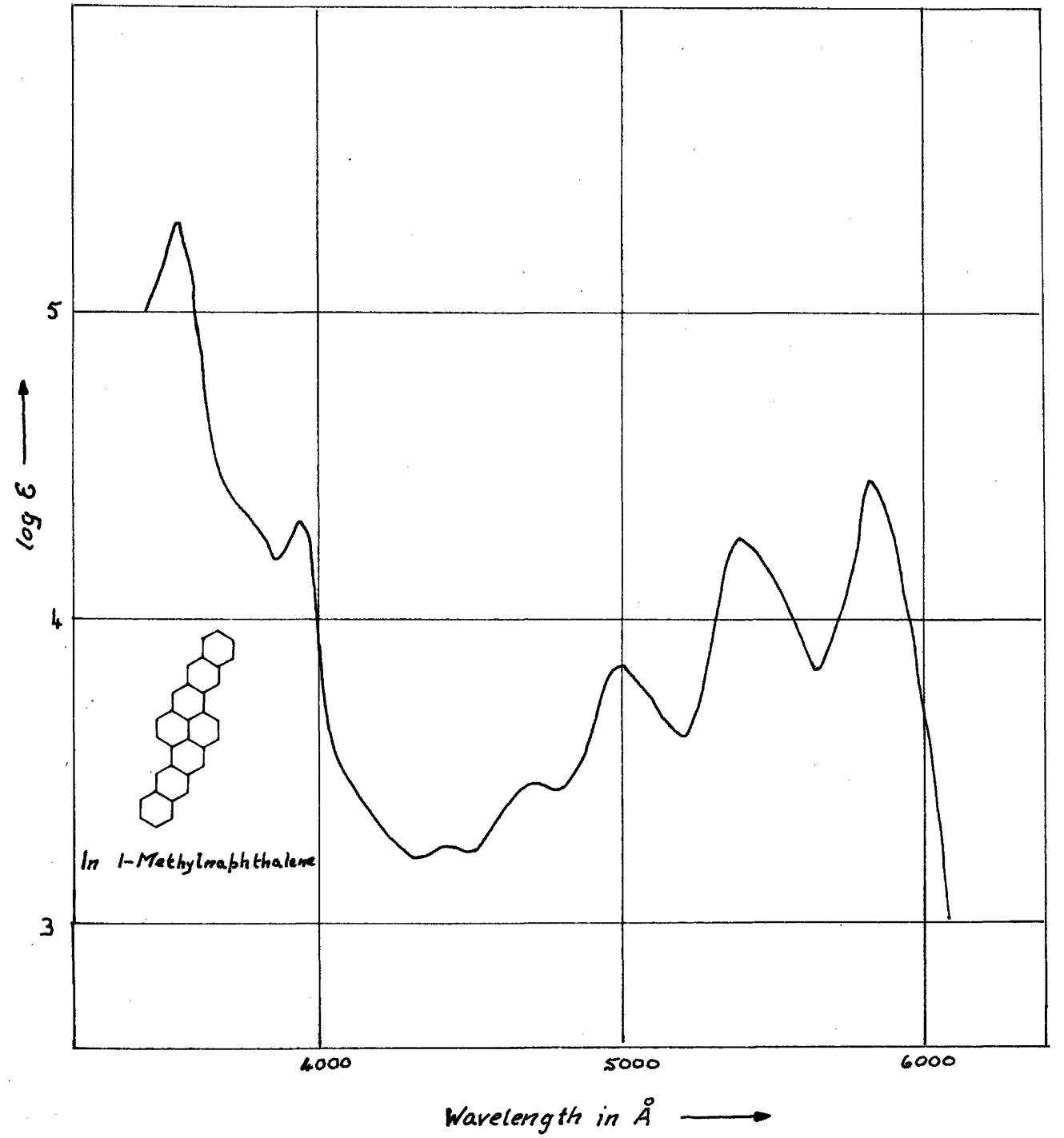
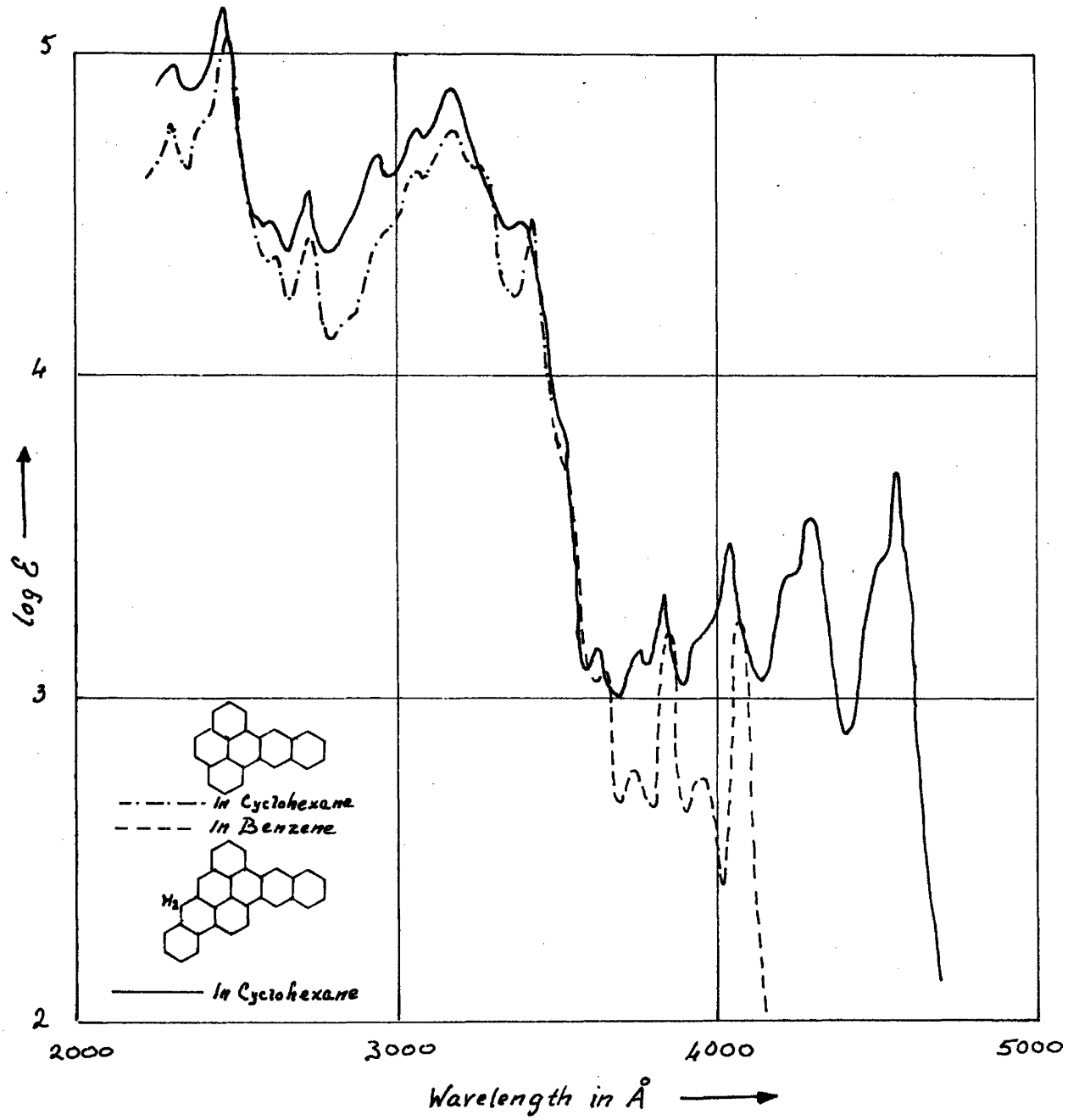

5
4
3
log ε
4000
5000
6000
Wavelength in Å
In 1-Methylnaphthalene

Fig. VIII


5
4
3
2
log ε
2000
3000
4000
5000
Wavelength in Å
In Cyclohexane
In Benzene
In Cyclohexane

EXPERIMENTAL.

1-(3'-CARBOXYNAPHTHOYL-2')-3,4,5,8,9,10-HEXAHYDROPYRENE (30).

To a solution of 3,4,5,8,9,10 hexahydropyrene (5 g) in tetrachloroethane (20 ml) was added a powdered mixture of 2,3-naphthalene dicarboxylic acid anhydride (4.4 g) and aluminium chloride (18 g) forming a violet red complex. After being shaken for one hour at 40°, this was decomposed with ice and hydrochloric acid. Steam distillation of the tetrachloroethane left a brown resin from which the acid (30) (4.9 g) was extracted with dilute ammonium hydroxide. It crystallised from xylene in colourless needles, m.p. 267°. (Found: C,82.94; H,5.67. $C_{28}H_{22}O_3$ requires C,82.93; H,5.46%.) 1-(3'-Carboxynaphthoyl-2')-3,4,5,8,9,10-hexahydropyrene dissolved in concentrated sulphuric acid to give a yellow brown solution which changed through violet, black and turquoise to blue.

ANTHRACENO-(1.2:2'.3')-PYRENE (29).

Keto-acid, (30), (1 g), zinc chloride (5 g) and sodium chloride (1 g) were heated to 320° for two minutes. Extraction with boiling water and ammonium hydroxide left a black tar which was crystallised from xylene giving crude anthracenopyrene (200 mg). A further quantity of (29) (75 mg) was obtained by concentration of the xylene liquors and treatment of the oil formed with copper powder at 300° under carbon dioxide. After sublimation from copper powder, the hydrocarbon crystallised from benzene in golden yellow plates, m.p. 285°, and dissolved in concentrated sulphuric acid to give a violet solution which changed through red to olive green. (Found: C,95.59; H,4.62. $C_{28}H_{16}$ requires C,95.42; H,4.58%.)

1,6-DI(2'-CARBOXYBENZOYL)-3,4,5,8,9,10-HEXAHYDROPYRENE (24).

3,4,5,8,9,10-Hexahydropyrene (11 g) was added to phthalic anhydride (62 g) and aluminium chloride (140 g) in tetrachloroethane (150 ml) at 60° forming a bright violet-red complex. After shaking for thirty minutes at 60° this was

decomposed with dilute hydrochloric acid. The tetrachloroethane was removed by steam distillation and the acidic products extracted with ammonium hydroxide. Fractional precipitation from boiling solution with acetic and hydrochloric acids afforded the acid (24) in various states of purity. It crystallised from acetic acid in short pale cream needles, m.p. 292°, which dissolved in concentrated sulphuric acid giving a green solution, becoming blue on standing. (Found: C,72.25; H,5.35. $C_{32}H_{24}O_6$ requires C,76.18; H,4.80%.)

1,6-DI(2'-CARBOXYBENZYL)-3,4,5,8,9,10-HEXAHYDROPYRENE (27).

The dicarboxylic acid, (24), (1.5 g) was refluxed for three days in 5% sodium hydroxide solution with zinc powder (activated with copper sulphate). Filtration and acidification of the filtrate gave a grey precipitate (1.05 g). Since this was very sparingly soluble in xylene and acetic acid and crystallisation from nitrobenzene afforded little purification, it was dissolved in alkali (charcoal) and gradually reprecipitated giving a white powder m.p. 303-305°. (Found: C,80.21; H,5.96. $C_{32}H_{28}O_4$ requires C,80.64; H,5.92%.) This

dissolved in concentrated sulphuric acid giving a violet solution, changing to red.

DINAPHTHO-(1.2:2'.3', 6.7:2".3")-PYRENE (23).

Dicarboxylic acid (27), (1 g), zinc chloride (9 g) and sodium chloride (1.8 g) were heated to 310°. At 280° the melt separated into two layers, the upper being red. Extraction with boiling water and ammonium hydroxide left a yellow-grey powder (0.95 g) which, after sublimation, crystallised from 1-methylnaphthalene in long, flat, pale yellow needles (0.55 g). Sublimation from copper powder gave pale pink needles, m.p. 428-429°, which did not dissolve in concentrated sulphuric acid. (Found: C,95.32; H,4.78. $C_{32}H_{18}$ requires C,95.49; H,4.51%.)

DI-(3,4,5,8,9,10-HEXAHYDRO-1-PYRENOYL) BENZENE-DICARBOXYLIC ACIDS ((31 AND (32)).

A powdered mixture of pyromellitic dianhydride (22 g) and aluminium chloride (75 g) was added to a solution of hexahydropyrene (45 g) in tetrachloroethane (150 ml) at 40° forming a violet-red complex. After shaking for one hour at 45°, this was decomposed with dilute hydrochloric acid and the

tetrachloroethane removed by steam distillation. Extraction with ammonium hydroxide left a yellow powder. Slow acidification of the hot solution of the ammonium salts gave a brown powder (36 g) which crystallised with difficulty from acetic acid as a light brown powder of unsharp m.p. (Found: C,76.65; H,5.46. $C_{42}H_{34}O_6H_2O$ requires C,77.28; H,5.56%.) It dissolved in concentrated sulphuric acid giving a blue solution which changed through violet to orange-red.

1.14,4.5,9.10,13.14-TETRABENZOHEPTACENE (33).

1. The yellow alkali-insoluble powder obtained from the above Friedel-Craft's reaction was crystallised from a large volume of xylene and sublimed from copper powder at 400° and 10^{-2} mm giving deep red needles (0.09 g). (Found: C,95.54; H,4.63%.) This hydrocarbon was identical with that obtained from (31) and (32) by a zinc chloride melt.

2. Powdered acids (31) and (32) (2 g), zinc chloride (10 g) and sodium chloride (2 g) were heated to 300°. Extraction with boiling water and ammonium hydroxide left a tar which sublimed

from copper powder in long deep red needles (0.12 g), m.p. 570°.[+] (Found: C,95.50; H,4.59. $C_{42}H_{22}$ requires C,95.79; H,4.21%.) It slowly dissolved in concentrated sulphuric acid giving a violet solution.

ATTEMPTED PREPARATION OF DINAPHTHO-(1.2:2'.3', 6.7:2".3")-PYRENE.

Hexahydropyrene (20.8 g), o-toluyl chloride (50 g) and aluminium chloride (34 g) were shaken in tetrachloroethane (100 ml) for 1 hour at between 40 and 50°. After decomposition of the claret-coloured complex with ice/dilute hydrochloric acid, the tetrachloroethane was removed by steam distillation. The resulting black resin was dissolved in xylene and the xylene solution washed thoroughly with dilute ammonium hydroxide. The xylene was removed by distillation and heating continued until the temperature of the residual liquid had reached 340°. Copper powder (3 g) was then added, and the temperature raised to 445° over a period of 30 minutes. Sublimation of the product

[+] Measured in a copper block using a Cambridge Instrument Co. Ltd. thermocouple thermometer.

gave initially large quantities of oil. Later fractions were crystallised from benzene affording short red needles (1.2 g). Further purification was effected by chromatography twice on Grade I alumina with benzene as eluent. The resulting hydrocarbon crystallised from petrol (b.p. 100-120°) in bright yellow silky needles, m.p. 257-8°. (Found: C,95.08; H,5.27%.) It dissolved slowly in concentrated sulphuric acid giving a green solution with a blue fluorescence.

3-METHYL-1 (OR 4)-NITRO-2-NAPHTHOIC ACID (43) OR (42).

2,3-Dimethylnaphthalene (20 g), manganese dioxide (2 g) and nitrobenzene (3 ml) were refluxed for 5 weeks in nitric acid (2.16 L, 7%). The remaining nitrobenzene was removed by steam distillation and, after cooling and filtration, the residue was extracted with dilute alkali. Acidification gave 3-methyl-1 (or 4)-nitro-2-naphthoic acid (1.5 g) which crystallised from xylene (charcoal) in short off-white needles m.p. 236°. (Found: C,62.62; H,4.38; N,6.07. $C_{12}H_9NO_4$ requires C,62.34; H,3.92; N,6.06%.) Its infra-red spectrum had absorption peaks at 1520 and 1360 cms^{-1}.

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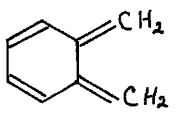
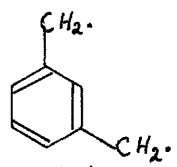
SECTION 3.

The possibility of the existence of p-quinonoid and m-quinonoid structures has already been discussed in Section 1. Consideration is now given to compounds derived from o-quinonoid structures.

The parent system, o-quinodimethane, "o-xylylene" or correctly, 1,2-dimethylenecyclohexadiene (1) can be written with one Kekulé structure; that is, in contrast to "m-xylylene" (2), all the bonding electrons can be paired. Thus "o-xylylene", like "p-xylylene", should be capable of existence as a hydrocarbon, rather than a diradical.



(1)

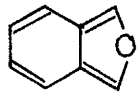


(2)

Some reactions involving "o-xylylene" have recently been reviewed[1]. In addition to those described a striking example is the synthesis of numerous adducts of "o-xylylene" in high yield by Alder and Fremery[2]. By generation of "o-xylylene" (and related compounds) in the presence of a dienophile they were able to "trap" it, as the adduct, before it could isomerise to benzocyclobutene or polymerise. Although the synthesis of benzocyclobutene has now stimulated much work, "o-xylylene" has not yet been

isolated, even in solution, and is known only as a reaction intermediate.

A considerable increase in stability, without appreciable destruction of the diene character of the molecule, is obtained if the two exocyclic double bonds are incorporated in a heterocyclic ring. The heterocyclic atom may be oxygen, sulphur, or nitrogen, derivatives of each system having been described.



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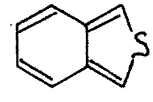

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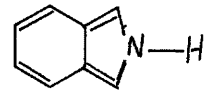
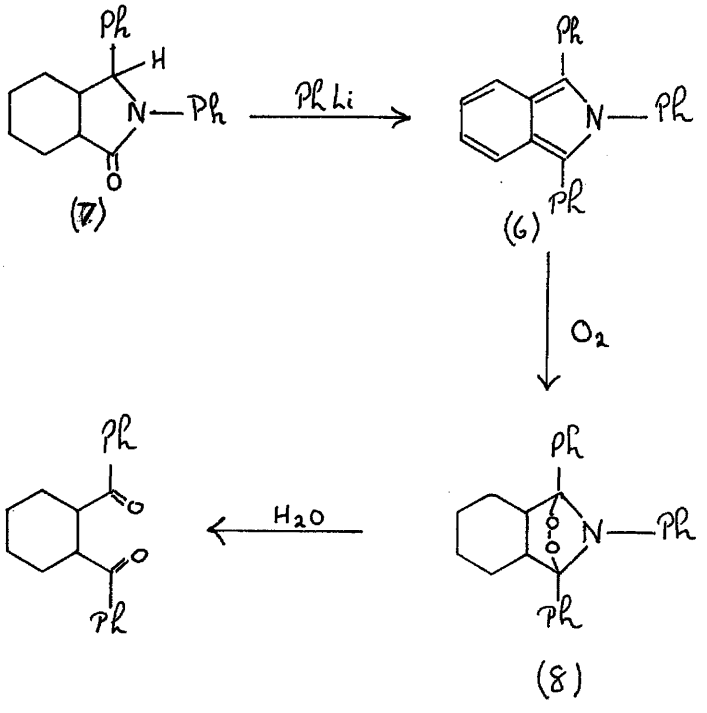


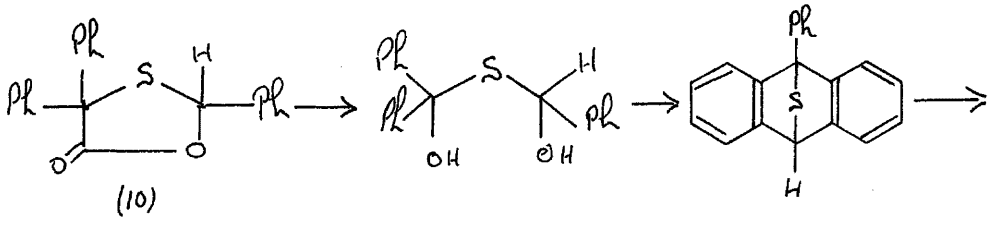
(5)

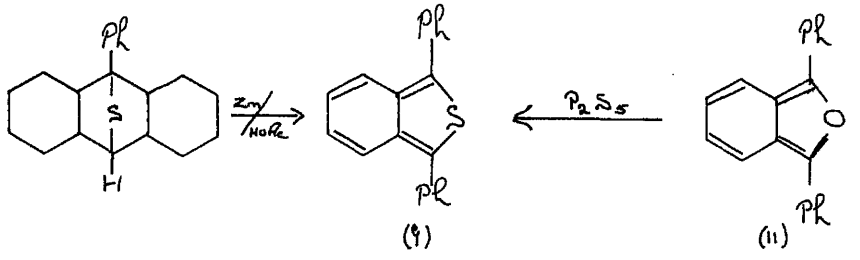
Although the compounds, isobenzofuran (3), isothianaphthene (4) and isoindole (5) have, themselves, not yet been isolated, phenyl derivatives of each have been known for some time. 1,2,3-Triphenylisoindole (6) was prepared[3] by treatment of 1,2-diphenylphthalimide (7) with phenyllithium. It is a pale greenish-yellow compound readily photooxidised

to 1,2-dibenzoylbenzene via the peroxide (8).



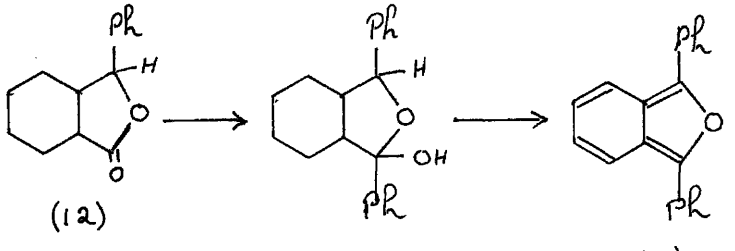
1,3-Diphenylisothianaphthene (9) was synthesised in 1922[4] from the lactone of α-hydroxybenzylthiobenzilic acid (10). This work was later confirmed by Dufraisse and Daniel[5] who also obtained it (9) by treatment of 1,3-diphenylisobenzofuran (11) with phosphorus pentasulphide.





(9) (11)

1,3-Diphenylisobenzofuran (11), the longest known and most widely investigated member of the series, was first synthesised by Guyot and Catel[6] in 1906 by dehydration of the tertiary alcohol (13) formed by treatment of 3-phenylphthalide (12) with phenylmagnesium bromide. It is a bright yellow compound whose solutions show a strong bluish fluorescence. It can be easily photo-oxidised and readily enters into addition reactions with dienophiles.

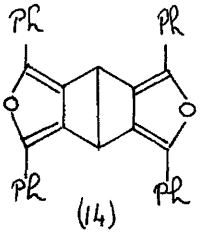


(12) (13) (11)

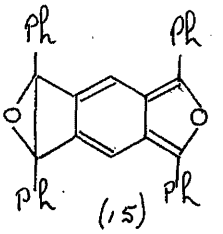
The absorption spectra of 1,3-diphenylisobenzofuran[7], 1,3-diphenylisothianaphthene[5] and

1,2,3-triphenylisoindole[3] have been measured, the wavelengths of the first band being 4150, 4000 and 3800 Å respectively. Thus the absorption of diphenylisobenzofuran is furthest advanced to the red and that of triphenylisoindole is least so. If this absorption band can be considered as being related to the p-bands of aromatic hydrocarbons[8] a relative measure would be obtained of the reactivity of the molecules giving an analogous series to that of furan, thiopene and pyrrole.

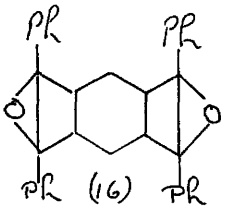
The ease with which the tertiary alcohol (13) could be dehydrated, with apparent destruction of the benzenoid system, led Clar and Fell[9] to carry out some preliminary experiments with a view to the simultaneous generation of the furan structure on both sides of a benzene nucleus. If this were possible, the resulting molecule could not be formulated in classical terms but would require, if uncharged structures, alone, were to be considered, a bond of the Dewar type, (14), (15) or, leaving the benzenoid sextet intact, (16).



(14)

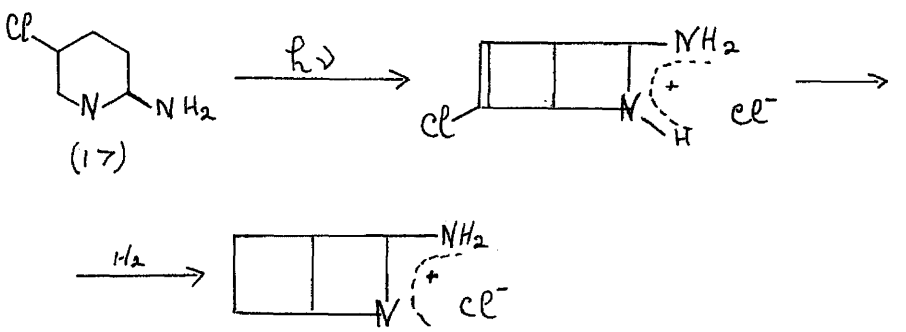


(15)



(16)

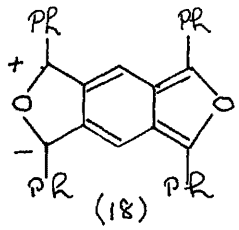
It has been suggested recently[10] that a bond of this type is formed on irradiation of 2-amino-5-chloropyridine (17).



(17)

Assuming the possibility of the existence of the molecule in a charged state, it could be represented by either (18) or (19) (corresponding to (15) and (16)). If (19) were a true representation, then this would imply that 1,3-diphenylisobenzofuran (11) itself should be represented by a charged structure, (20), leaving

the sextet undisturbed.



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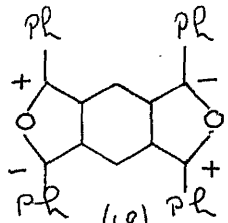
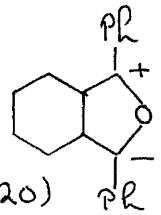
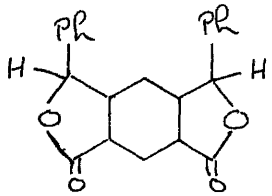


(19)

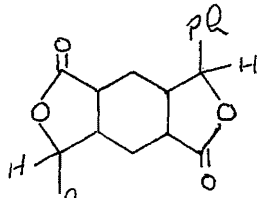


(20)

The approach adopted by Clar and Fell was analogous to that of Guyot and Catel[6].



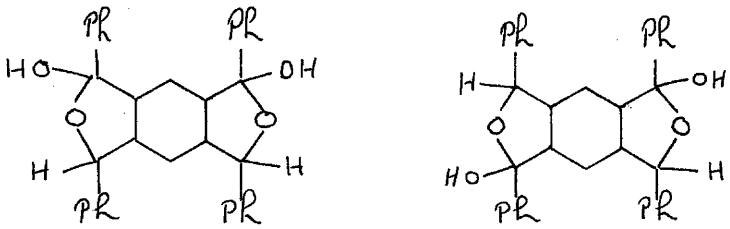
(22)



(21)

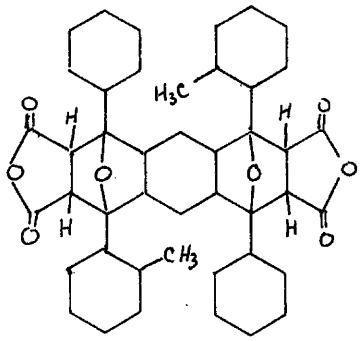
The two isomeric lactones (21) and (22), obtained by reduction of the corresponding dibenzoylphthalic acids[11], were easily separated by fractional crystallisation. These lactones reacted with phenylmagnesium bromide affording an uncharacterised alcohol (probably (23)), which, when dehydrated by heating above its melting point or by boiling with concentrated hydrochloric acid in acetic acid, gave bright yellow material with absorption (4100 Å) similar to that of diphenylisobenzofuran (4150 Å).

Attempted purification of this substance gave only a stable colourless compound which showed neither carbonyl nor hydroxyl absorption in the infra-red.

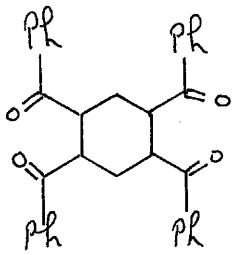


(23)

Reaction of the lactone (21) with o-tolylmagnesium bromide similarly led to unidentified yellow material from which, however, a maleic anhydride adduct was obtained corresponding to (24). Solutions of this yellow substance in contact with perchloric acid became bright green and developed an absorption band at 7000 Å in addition to the one at 4100 Å which was reduced in intensity.

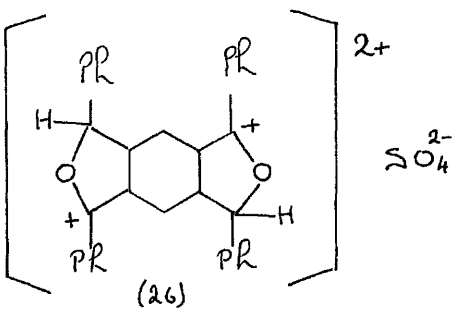


(24)



(25)

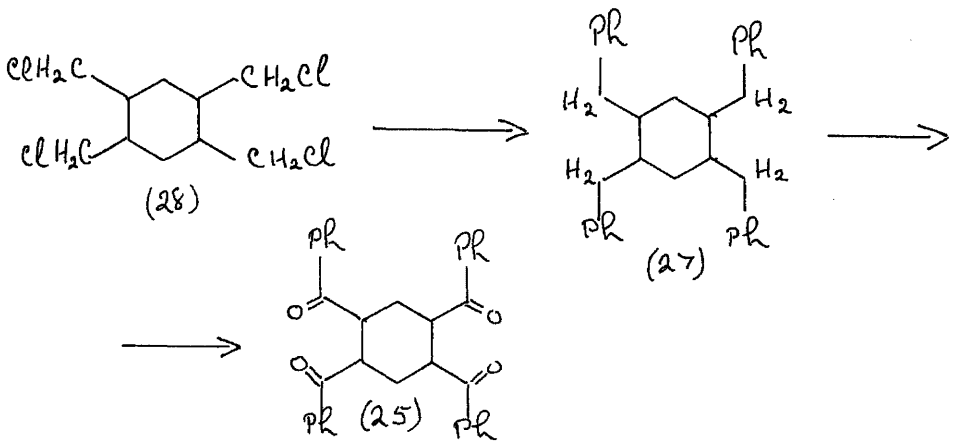
In the present case, when work on this project was started, it was noticed that reduction of 1,2,4,5-tetrabenzoylbenzene (25) with copper powder and concentrated sulphuric acid gave rise to bright greenish-blue solutions with absorption of an apparently similar type to that described above. Since reduction of 1,2-dibenzoylbenzene with zinc dust and acetic acid[12,13] (or with activated zinc and ethanolic sodium hydroxide[14]) was known to give 1,3-diphenylisobenzofuran, it was possible that a cation such as (26) might exist under the strongly acidic conditions present. Accordingly an investigation of the products of reduction of (25) with copper and sulphuric acid was carried out.



(26)

1,2,4,5- Tetrabenzoylbenzene (25) has been prepared in good yield by oxidation of 1,2,4,5-tetrabenzylbenzene[15] (27). The two-step synthesis consisted of a ferric chloride catalysed condensation

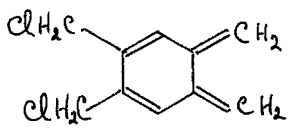
of 1,2,4,5-tetrakis-(chloromethyl)-benzene (tetrachlorodurene) (28) with benzene, followed by oxidation with chromium trioxide in acetic acid.



The starting material, tetrachlorodurene, has been obtained both from durene, by chlorination with phosphoruspentachloride[16], and from technical xylene by chloromethylation[17] followed by direct chlorination of the resulting dichlorodurene[15, 17]. Since durene, itself, was available, tetrachlorodurene was prepared from it by direct chlorination in boiling carbontetrachloride under irradiation by a mercury arc lamp.

Considerable difficulty was experienced with the condensation of (28) with benzene. At room temperature very little reaction appeared to take place even when freshly dried ferric chloride[19] was

used. Heating the mixture initiated the condensation, but no tetrabenzylbenzene was isolated from the tar produced. It was found that tetrachlorodurene reacted vigorously with phenyllithium in ether-solution with the formation of an insoluble yellow polymer. It is probable that the phenyllithium first causes dehalogenation to an "o-xylylene" derivative such as (29), which would polymerise immediately under the conditions of the reaction. Similar polymer formation has been recorded by the treatment of w,w'-dihalogeno-o-xylene with magnesium[20] and with zinc[2].

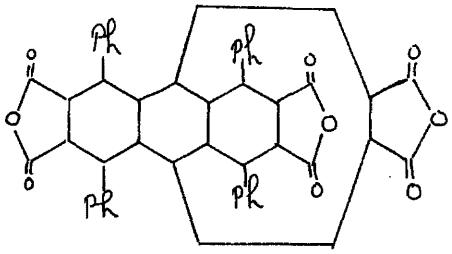


(29)

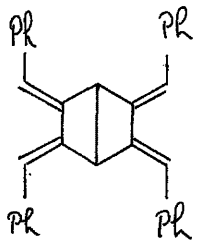
Tetrachlorodurene, however, was converted smoothly to tetrabenzylbenzene (27) by reaction with phenylmagnesium bromide. No polymerisation was observed and the yields obtained compare favourably with those claimed for the Friedel-Crafts condensation[15].

Attempts to obtain an adduct of tetrabenzylbenzene and maleic anhydride by prolonged treatment

with chloranil in boiling maleic anhydride were unsuccessful. The isolation of any such adduct, e.g. (30) would have necessitated either the intermediate formation of a "Dewar" bond (31) or a two-step reaction involving derivatives of "o-xylylene".



(30)



(31)

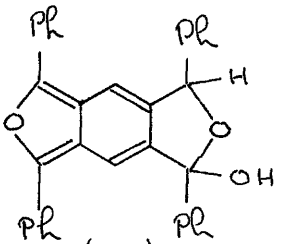
The oxidation of tetrabenzylbenzene was carried out essentially as described in the literature[15], halving the reaction time resulted in only a small reduction in yield.

The green colour produced by reduction of tetrabenzoylbenzene with copper powder in concentrated sulphuric acid persisted on infinite dilution with acetic anhydride, although it was immediately discharged on dilution with water. Its absorption spectrum is shown in fig. I. (Log E calculated from the tetrabenzoylbenzene).

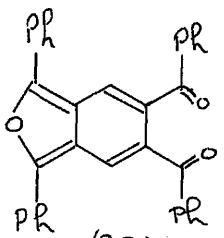
Dilution of the green sulphuric acid solution with a large excess of water precipitated a greenish-yellow solid from which a bright orange compound was obtained by crystallisation from benzene. No other solid material could be isolated. The best yields occurred with reductions lasting between three and five minutes, an increase in reduction time causing a decrease in the quantity of orange compound obtained.

The orange reduction product gave bright yellow solutions with a strong greenish-blue fluorescence. Its ultraviolet absorption spectrum (fig. II) showed a general similarity to that of diphenylisobenzofuran. It dissolved in concentrated sulphuric acid giving a green solution whose absorption spectrum (fig. I) was almost identical with that of the initial reduction medium. By treatment with maleic anhydride in xylene an adduct was obtained which contained one molecule of maleic anhydride. This adduct was rather unstable, dissociation occurring in boiling benzene or xylene. At room temperature, a solution of the adduct in dilute potassium hydroxide slowly decomposed with precipitation of the original orange material.

This decomposition was accelerated as the temperature was raised.

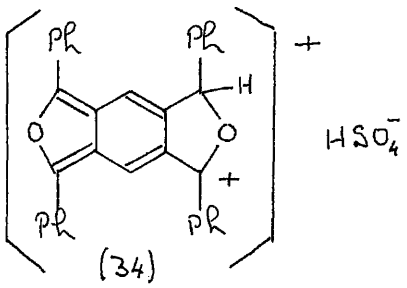


(32)



(33)

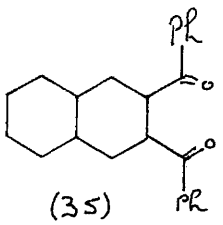
The preceding evidence and the analytical data for both the orange compound and its adduct would support either (32) or (33) as the structure of the reduction product. The formation of (32) could be accounted for by initial reduction to (34) which, on addition of water would form (32). This would also explain the reversability of the colour change from concentrated sulphuric acid to water since simple dehydration in the acid would reform (34).



(34)

A study of the infra-red absorption spectrum revealed no absorption in the hydroxyl region. In the carbonyl region, however, there were twin absorption peaks at 1645 and 1660 cms^{-1}. The

occurrence of carbonyl absorption at two frequencies in an apparently symmetrical molecule may at first seem rather unusual. It could possibly be due to the presence of two such large groups (benzoyl) on adjacent atoms of an aromatic ring causing appreciable distortion. In confirmation of this an examination of the spectra of 2,3-dibenzoyl-naphthalene (35)+ and 1,2,4,5-tetrabenzoylbenzene (25) revealed, in both cases, twin absorption peaks at 1660 and 1680 cms^{-1} for dibenzoylnaphthalene and at 1655 and 1680 cms^{-1} for tetrabenzoylbenzene.

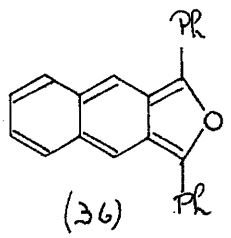


(35)

The orange reduction product dissolved in acetic anhydride in the presence of a trace of concentrated sulphuric acid giving a blue solution which did not react with maleic anhydride. It reacted with an excess of hydrazine hydrate in hot acetic acid solution, the colour changing from yellow, through green to blue. No crystalline product could be isolated from this reaction. Dilution with

+ vide infra.

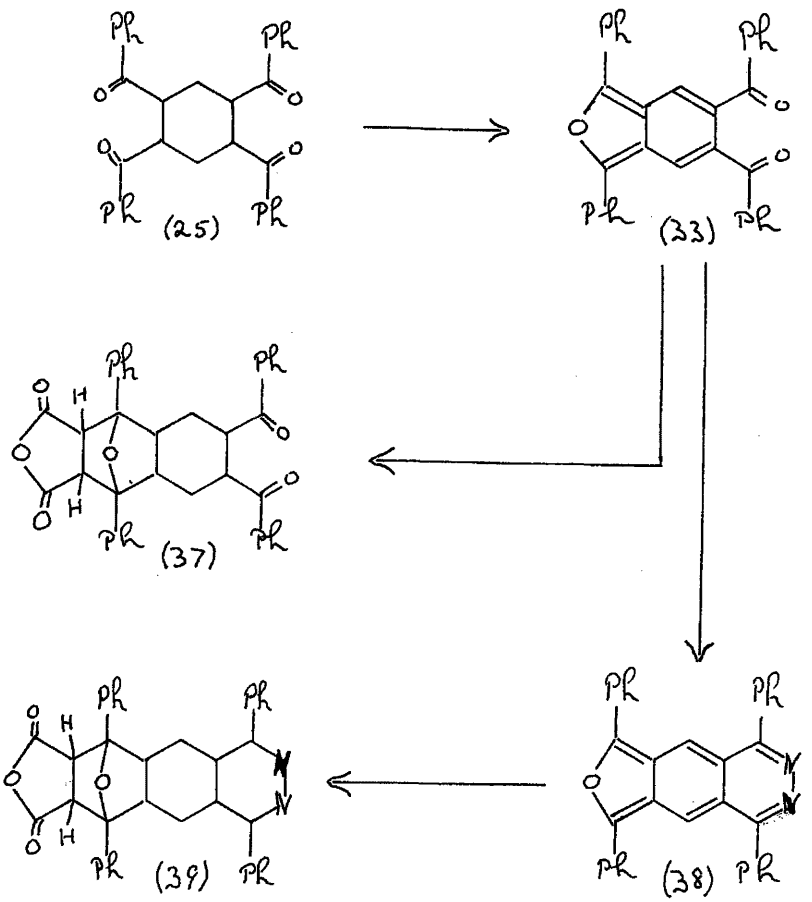
water formed a violet precipitate. All attempts to crystallise this violet compound have failed. It formed bright red solutions with red fluorescence which were readily photo-oxidised on exposure to light. Photo-oxidation also occurred in the solid state, although more slowly, several hours' exposure to diffused daylight being necessary. Its ultra-violet absorption spectrum (fig. III) shows a striking similarity to that of 1,3-diphenyliso-naphthofuran (36) (the synthesis of which is described later). This is a valid comparison since replace-ment of a carbon atom by a nitrogen atom in a polycyclic system causes little change in absorption spectrum, e.g. anthracene and acridine have very similar spectra. A stable crystalline adduct was readily formed by treatment with maleic anhydride.



(36)

The above reactions and infra-red spectral data weigh heavily in favour of 5,6-dibenzoyl-1,3-diphenylisobenzofuran (33) for the structure of the orange compound. Thus the complete reaction

scheme may be written as follows:-



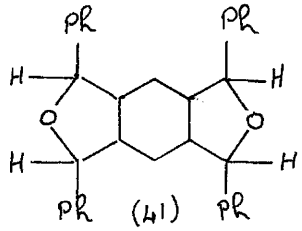
Satisfactory analytical figures have been obtained for both the 1,3,5,8-tetraphenyl-6,7-diaza-(2',3')-isonaphthofuran (38) and its maleic anhydride adduct (39).

The green colour produced on reduction of 1,2,4,5-tetrabenzoylbenzene (25) with copper in concentrated sulphuric acid would appear, therefore, to be caused by protonation of the resulting

5,6-dibenzoyl-1,3-diphenylisobenzofuran (33) in the sulphuric acid rather than to the presence of a charged species derived from a "Dewar" bond. 2,3-Dibenzoylnaphthalene (35) and 1,2,4,5-tetrabenzoylbenzene (25) both dissolve in concentrated sulphuric acid giving solutions which show strong long-wave absorption (fig. IV). The failure of 5,6-dibenzoyl-1,3-diphenylisobenzofuran (33) to react with maleic anhydride in acetic anhydride solution in the presence of sulphuric acid could result either from the known instability of the adduct (37) or from the structure of the protonated molecule, the isobenzofuran complex being not necessarily retained; e.g. protonation at a carbonyl group could give rise to a cation containing a p-quinonoid system of double bonds (40).

When the reduction of tetrabenzoylbenzene (25) was carried out for a much longer period (two to three hours), in addition to the dibenzoyl-diphenylisobenzo-

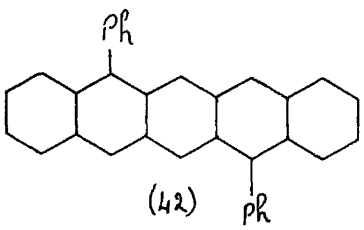
furan (33), a colourless compound was isolated. This was less soluble in benzene than (33) and showed neither hydroxyl nor carbonyl absorption in the infra-red. Analytical figures are compatible with this compound being 5:6-(2',3'-diphenyl-(3':4')-tetrahydrofurano)-1,3-diphenylphthalan (41). 1,3-Diphenylisobenzofuran can be reduced with sodium and alcohol to 1,3-diphenylphthalan.



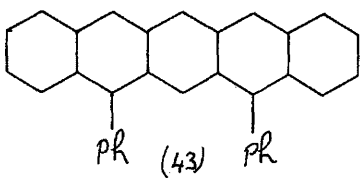
(41)

Although chemically stable it decomposed on sublimation. The sublimate, a red oil, dissolved in benzene giving a magenta coloured solution which exhibited a strong red fluorescence, and had absorption bands in the visible region at 5110, 5460 and 5910 Å. Although it would seem probable that the compound responsible for these absorption bands would be 5,11-diphenylpentacene (42) or 5,7-diphenylpentacene (43), this has not been confirmed since all attempts to isolate a pure sample from the considerable quantity of oil produced by the sublimation have been unsuccessful. Photo-oxidation

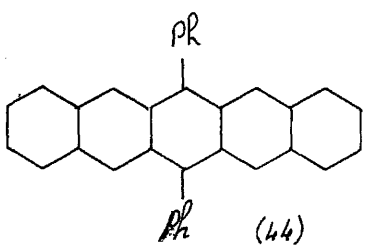
occurred readily on exposure of solutions to light and chromatography brought about immediate decomposition. 6,13-Diphenylpentacene (44) has been described[21] and has absorption bands at 5090, 5470, and 5920 Å (solvent not stated).



(42)



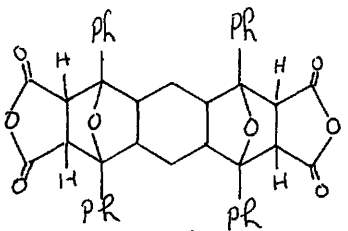
(43)



(44)

In an effort to gain some insight into the mechanism of the reduction an attempt was made to obtain a compound, or compounds, corresponding to a stage of reduction intermediate between the dibenzoyldiphenylisobenzofuran (33) and the double phthalan (41). A reduction of tetrabenzoylbenzene (25) lasting for one and a quarter hours yielded only 5,6-dibenzoyl-1,3-diphenylisobenzofuran (33) As before, concentration of the mother liquors from the crystallisation of this compound afforded a red oil. This oil was decolourised immediately with maleic anhydride but,

although non-crystalline material was obtained for which the analytical figures corresponded to the double adduct (45), this does not constitute sufficient evidence for the existence of a compound such as (18).



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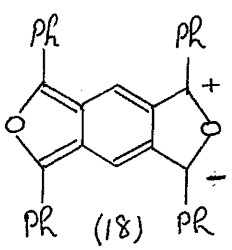
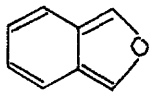


(18)

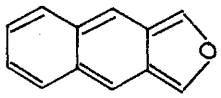
The ease with which dimerisation and photo-oxidation occur in molecules of the diphenylisobenzofuran type led Guyot and Catel[6] and later Adams and Gold[7] to suggest the facile formation of diradicals. Although in the strongly acid conditions present in the reduction of tetrabenzoylbenzene there exists the possibility of the stabilisation of a radical form of the molecule as a dication (e.g. (26)), no conclusive evidence of this has been found.

1,3 - DIPHENYL - (2':3') - ISONAPHTHOFURAN.

A unit linear extension of the ring system of isobenzofuran (3) would lead to (2':3')-isonaphthofuran (46).



(3)

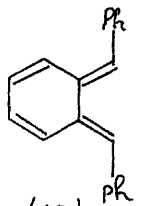


(46)

Without resort to formal charges or to a radical form, this molecule could contain no benzenoid ring, the only possible classical structure being that shown, (46).

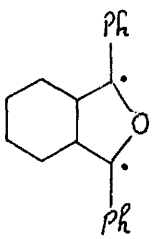
If, in the furan ring, the oxygen atom could donate two electrons, retaining no hold on them, then a true aromatic sextet would be formed, comparable with that of benzene. On linear anellation of rings, two electrons would be capable of migration[22] from the heterocyclic ring throughout the whole ring system giving a series equivalent to the acene, i.e. isobenzofuran (3) and isonaphthofuran (46) would show stability and properties similar to naphthalene and anthracene respectively. This is obviously not the

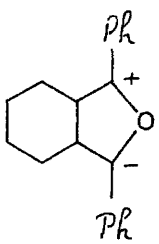
case. At the other extreme, if the oxygen atom took no part in the conjugation diphenylisobenzofuran (11) would be expected to show similar stability to w,w'-diphenyl-o-xylylene (47). Again this is not borne out in practice.



(47)

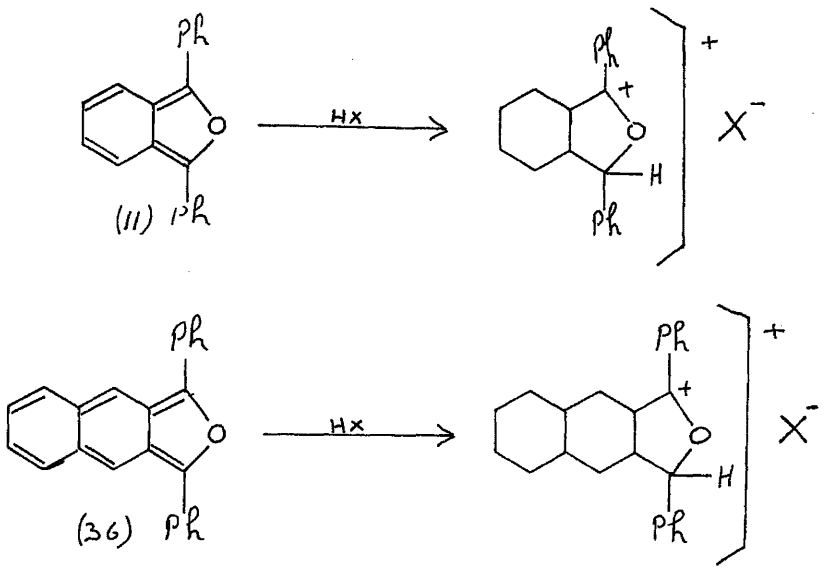
Alternatively, forsaking classical bond structures, the furan ring could be written as a diradical or with formal charges as was suggested by Adams and Gold[7].



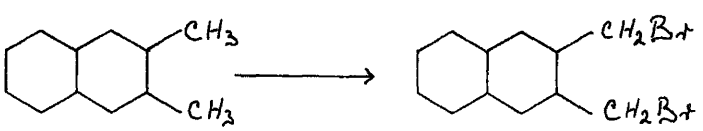


In this case the molecule would gain a benzenoid ring. It has already been shown[23] that there exists a considerable driving force for the formation of benzenoid rings in polycyclic hydrocarbons, even to the extent of polerisation of the molecule. If this could be extended to include heterocyclic systems also then it might be expected that an increase in stability would result from the polerisation of molecules such

as 1.3-diphenylisobenzofuran (11) and 1,3-diphenyl-(2':3')-isonaphthofuran (36).

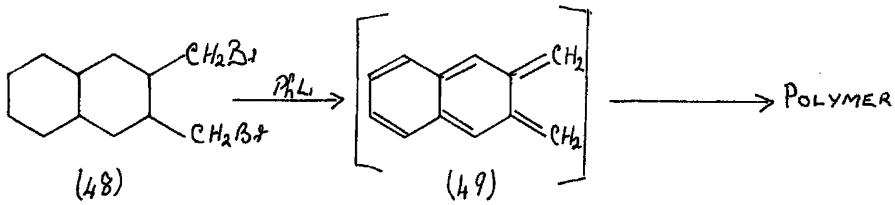


Until this year, apart from polycyclic aromatic hydrocarbons of the acene series, no compound was known which contained the 2,3-naphthoquinonoid structure. It was hoped, therefore, that the then unknown diphenylisonaphthofuran (36) would be obtained by reduction of 2,3-dibenzoylnaphthalene (35) with copper powder in sulphuric acid solution.



(48)

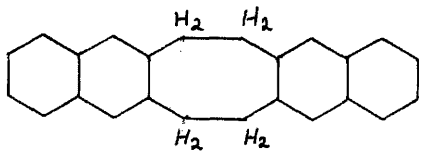
Bromination of 2,3-dimethylnaphthalene by N-bromosuccinimide in boiling carbon tetrachloride in the presence of benzoyl peroxide, and under irradiation by a mercury arc lamp, gave 2,3-bis-bromomethylnaphthalene (48) in 46% yield. With the exception of the use of the mercury arc lamp this preparation is similar to that of the 2,7-isomer (yield, 49%) described by Baker, Glocking and McOmie[26]. As with tetrachlorodurene, phenyllithium reacted vigorously with 2,3-bisbromomethylnaphthalene (48) forming polymeric material. It seems likely that the mode of polymerisation is similar in both cases; in this case the reaction intermediate would be (49).



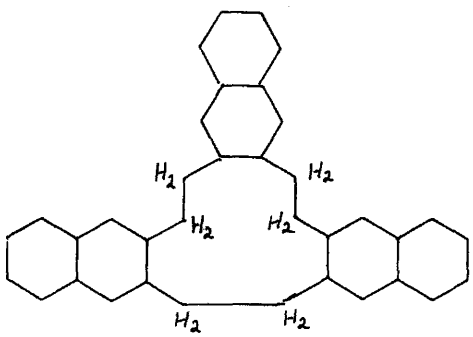
(48) (49)

The polymer formed from (48) was a white powder sparingly soluble in boiling xylene. That formed from tetrachlorodurene (28) was a yellow-brown solid having the consistency of cheese when moistened with solvents. It was completely insoluble in all solvents tried. These properties are consistent with the

fact that tetrachlorodurene is capable of polymerising in two directions, whereas bisbromomethylnaphthalene can form only a straight chain polymer or cyclic molecules of relatively low molecular weight such as (50) or (51), analogous to those obtained by Baker etal.[27] on treatment of o-xylylene dibromide with sodium.



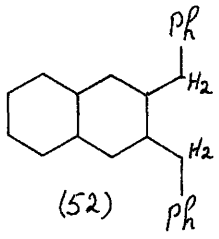
(50)



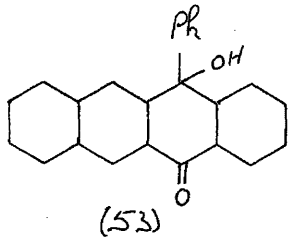
(51)

Both polymers decomposed on sublimation. The sublimates dissolved in benzene giving highly coloured solutions having many absorption bands in the visible region. No attempt was made to isolate any of the products. Treatment of 2,3-bisbromomethylnaphthalene with phenylmagnesium bromide in boiling benzene afforded 2,3-dibenzylbenzene (52) in 50% yield.

On treatment of 2,3-dimethylnaphthalene with cromium trioxide in aqueous acetic acid at room temperature,[28] or with hydrogen peroxide at 80%,[29] a 60-80% yield of 2,3-dimethyl-1,4-naphthoquinone results. Since both cromium trioxide and hydrogen peroxide, therefore, seemed entirely unsuitable for the oxidation of 2,3-dibenzylnaphthalene to 2,3-dibenzoylnaphthalene, and since dilute nitric acid was known to cause considerable nitration[30], attempts were made to carry out the oxidation with selenium dioxide. Refluxing with selenium dioxide in nitrobenzene, or heating with selenium dioxide and water at 180° in a sealed tube, afforded a compound isomeric with 2,3-dibenzoyl-naphthalene. It had an absorption peak at 1660 cms^{-1} in the infra-red.



(52)



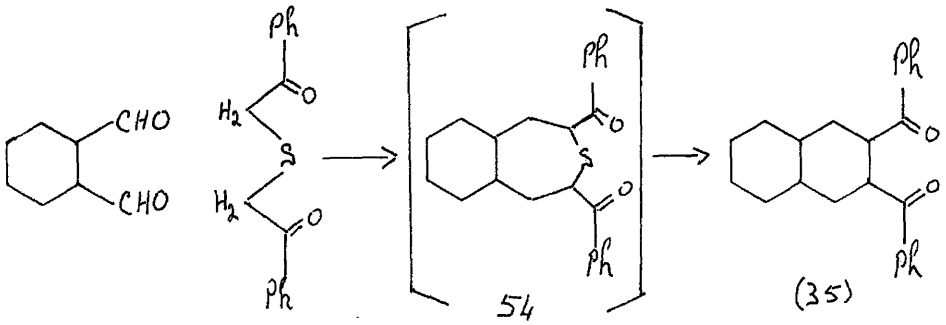
(53)

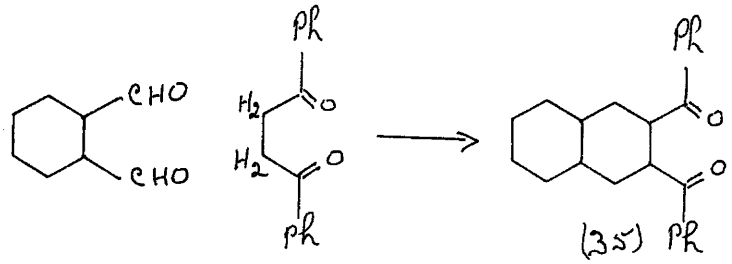
A preliminary qualitative investigation would appear to indicate (53) as the structure of this compound. Oxidation of dibenzylnaphthalene with selenium dioxide in acetic acid gave material having absorption at 1655 and 1720 cms^{-1} (acetate absorbs between 1730 and 1717 cms^{-1}). Hydrolysis of this with dilute

alkali yielded a compound identical with that formed in the higher temperature oxidations. Reduction of the oxidation product with zinc dust in acetic acid gave bright yellow material with sharp absorption bands at 4830, 4530, 4280 and 4050 Å in benzene which is in accord with the spectrum of phenyltetracene.

An unsuccessful attempt was made to condense cis-dibenzoylethylene with 1,2-bisbromomethylbenzene (o-xylylene dibromide) under conditions similar to those used by Alder and Fremery[2] in the preparation of adducts of "o-xylylene".

2,3-Dibenzoylnaphthalene has now been described by Loudon and Sloan[31]. They obtained it in 57% yield by condensation of o-phthalaldehyde with diphenacyl sulphide without detecting the intermediate thiepin (54). In the present case, it was found that o-phthalaldehyde would condense with 1,2-dibenzoylethane (diphenacyl) affording 2,3-dibenzoyl-naphthalene (35) in 75% yield.





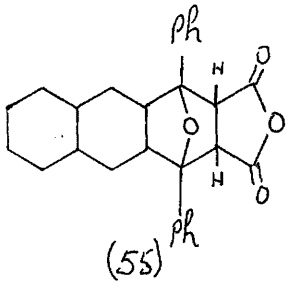
(35)

Bright red solutions were immediately formed by reduction of 2,3-dibenzoylnaphthalene with zinc dust in acetic acid. Over-reduction, however, occurred readily and quenching the reaction with water after various reduction times gave 1,3-diphenyl-(2',3')-isonaphthofuran (36) of only low purity. The most efficient method of reduction of (35) to (36) was found to be by treatment with copper powder in concentrated sulphuric acid. The reaction was accompanied by a very pronounced colour change. The deep green solution of dibenzoylnaphthalene (35) in sulphuric acid became suddenly orange-yellow about 60 seconds after addition of copper powder. Terminating the reaction at this stage by dilution with water gave a bright violet-red precipitate of diphenylisonaphthofuran (36). It gave solutions which were bright red with a red fluorescence and whose absorption spectrum is shown in fig. III.

These solutions decolourised rapidly on exposure to light and, on standing for several hours in the absence of light, reoxidation occurred to 2,3-dibenzoylnaphthalene (35). Because of the instability of diphenylisonaphthofuran (36) in solution it could not be recrystallised. It dissolved in concentrated sulphuric acid giving orange-yellow solutions (4000 Å) which were very much more stable than solutions in organic solvents. In the absence of light diphenylisonaphthofuran (36) was stable in the solid state.

After reduction of dibenzoylnaphthalene (35) with copper powder and sulphuric acid for two hours a considerable proportion of the product still consisted of the diphenylisonaphthofuran (36). This is in marked contrast to the reduction of (35) with zinc dust in acetic acid or with zinc dust in pyridine and acetic acid.

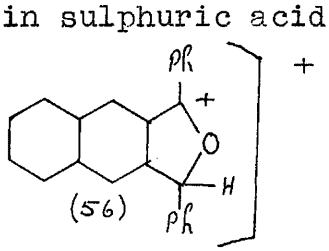
Diphenylisonaphthofuran (36) reacted immediately with maleic anhydride forming the colourless adduct (55).



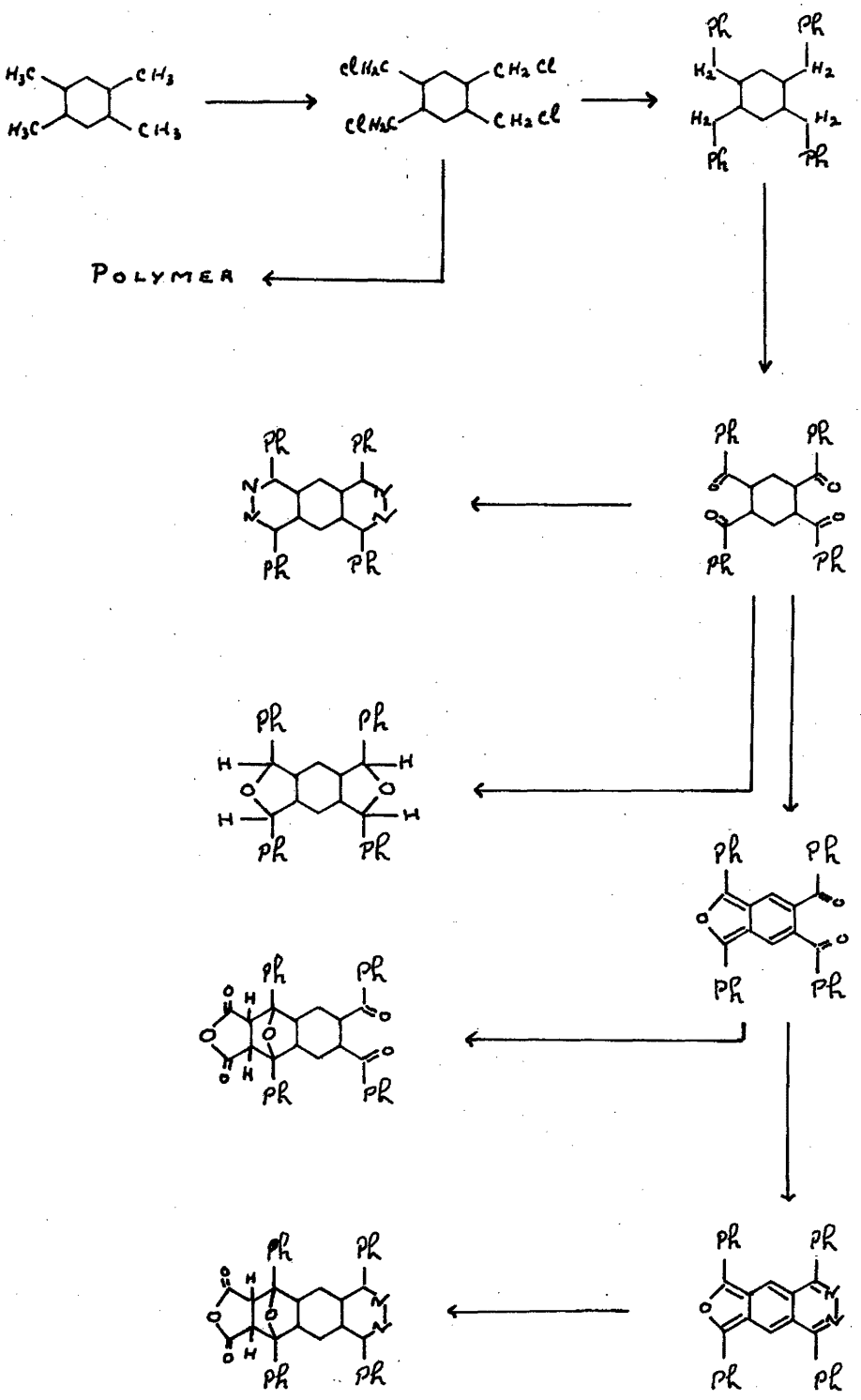
(55)

A description of the synthesis and properties of diphenylisonaphthofuran (36) by Cava and Van Meter has now been published[24]. The route followed by them was similar to that of Guyot and Catel[6] in the original synthesis of 1,3-diphenylisobenzofuran and the yields obtained were good, the overall yield from 3-benzoyl-2-naphthoic acid[25] being 45%. They also were unable to recrystallise the compound. A comparison of the absorption spectra of 2,3-dibenzoylnaphthalene, its reduction product and 1,3-diphenyl-(2',3')-isonaphthofuran[24], shows that, although not pure, the reduction product of dibenzoylnaphthalene (35) contains a relatively high proportion of diphenylisonaphthofuran (36). This is also borne out by the preparation, in 58% yield, of the maleic anhydride adduct (55).

The rapid initial reduction of (35), the resistance of diphenylisonaphthofuran (36) to further reduction in concentrated sulphuric acid, and the very strong violet shift in absorption on changing from hydrocarbon solvents to sulphuric acid (5520 to 4000 Å) would seem to indicate the prescence in sulphuric acid of a species such as (56).



(56)


POLYMER

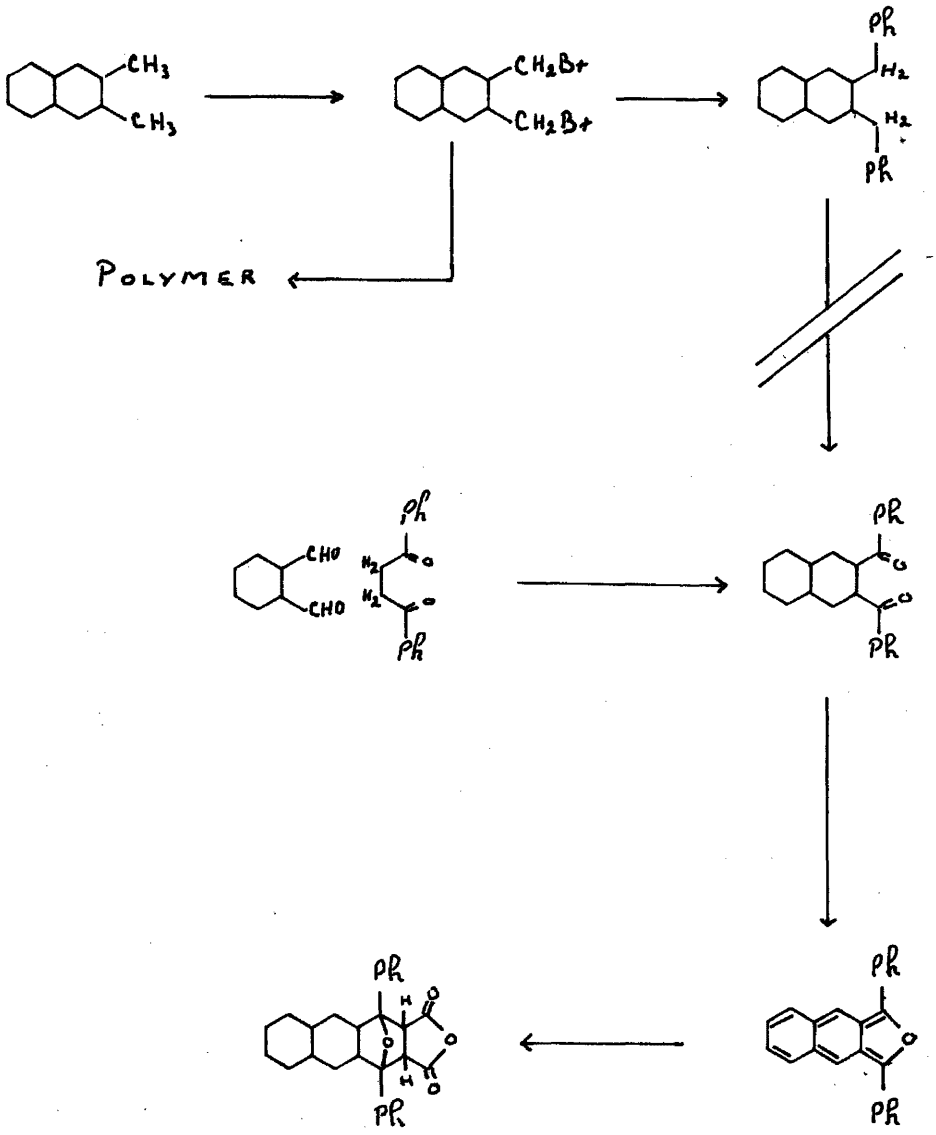

CH3
CH3
CH2Br
CH2Br
Ph
H2
H2
Ph
POLYMER
CHO
CHO
H2
H2
Ph
Ph
Ph
Ph
Ph
Ph
H
H
O
O
O
O
Ph
Ph

Fig. I

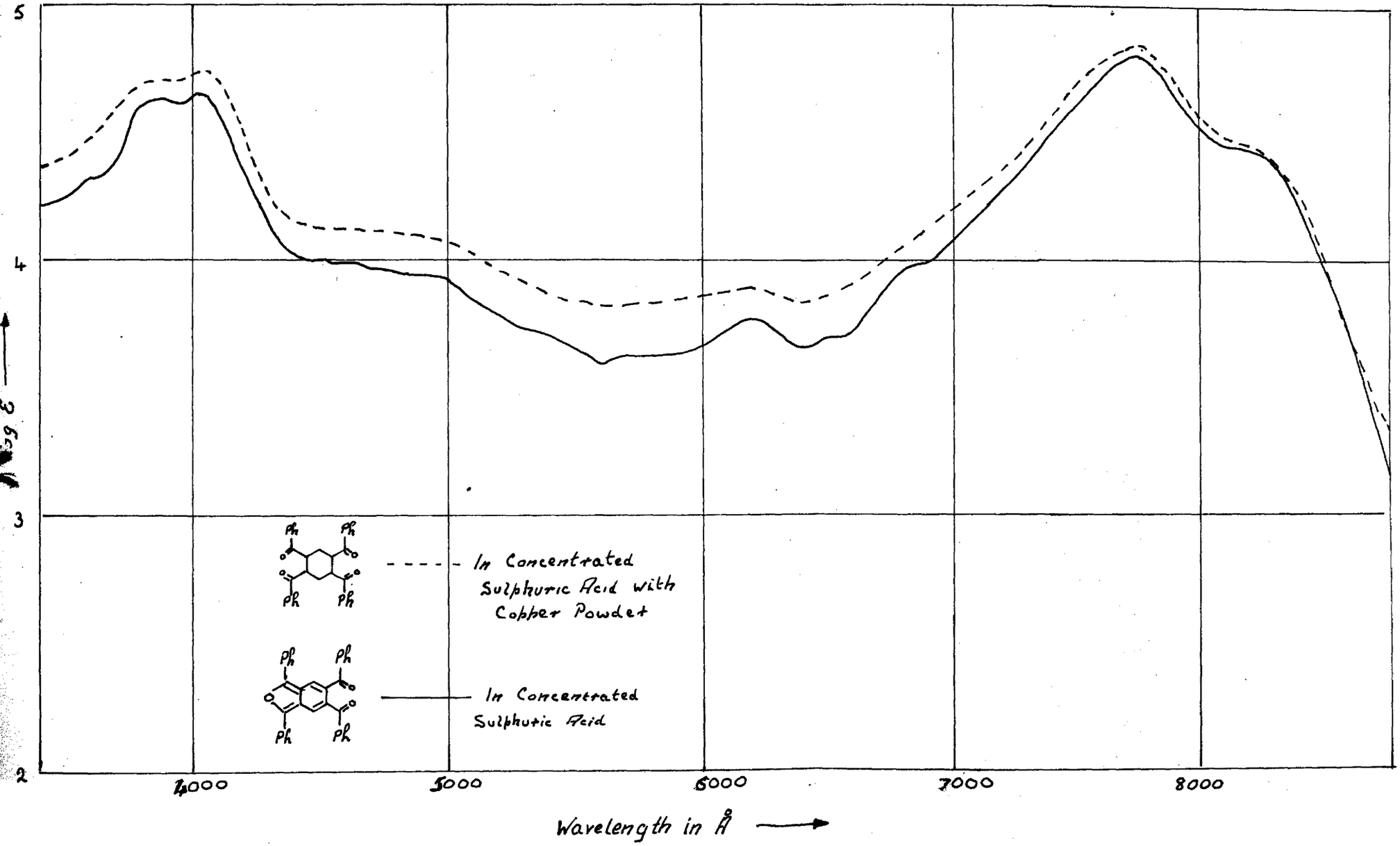

5
4
3
2
log ε
4000
5000
6000
7000
8000
Wavelength in Å
Ph
Ph
Ph
Ph
In Concentrated Sulphuric Acid with Copper Powder
In Concentrated Sulphuric Acid

Fig. II

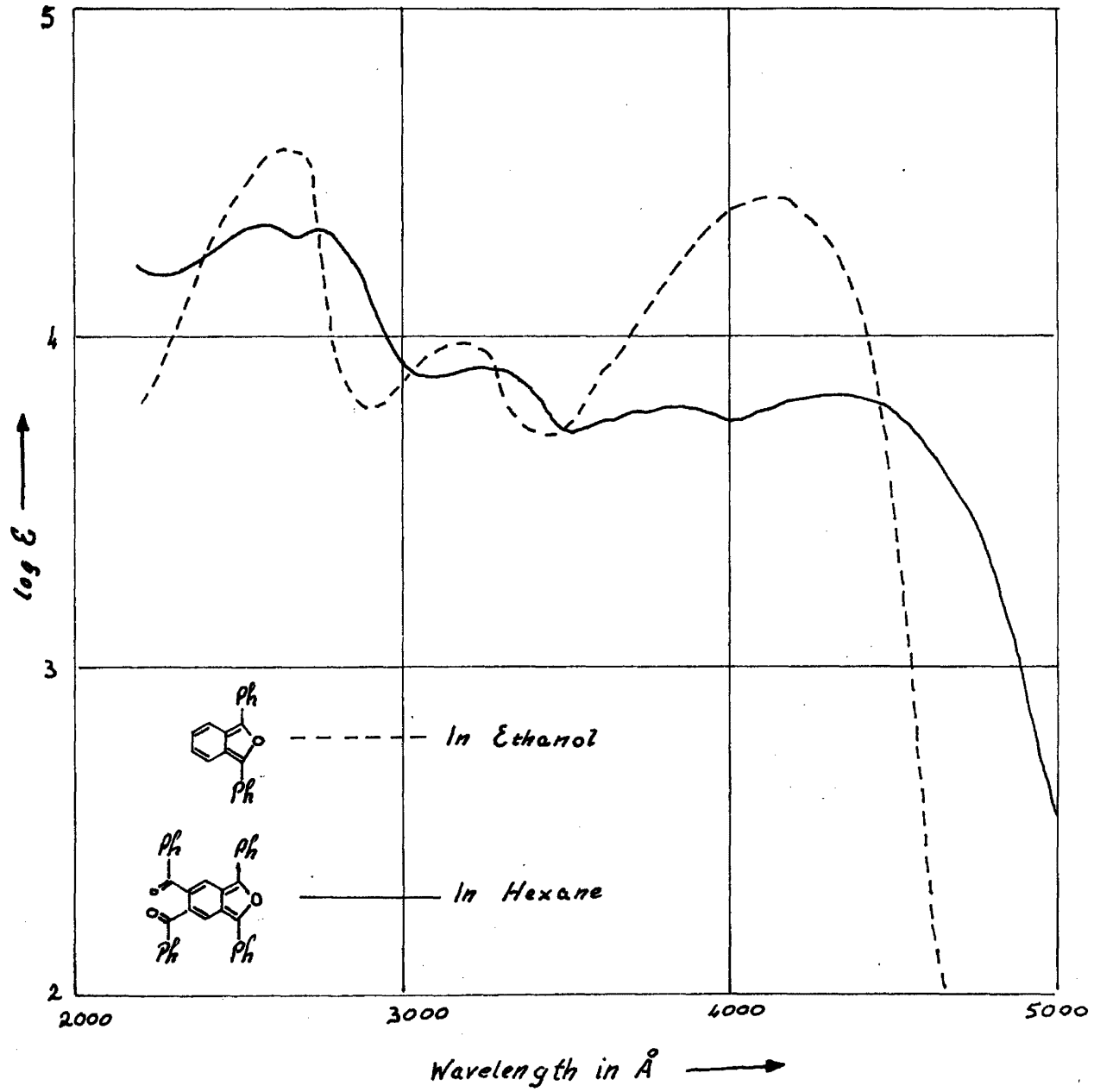

5
4
3
2
log ε
2000
3000
4000
5000
Wavelength in Å
In Ethanol
In Hexane
Ph
O

Fig. III

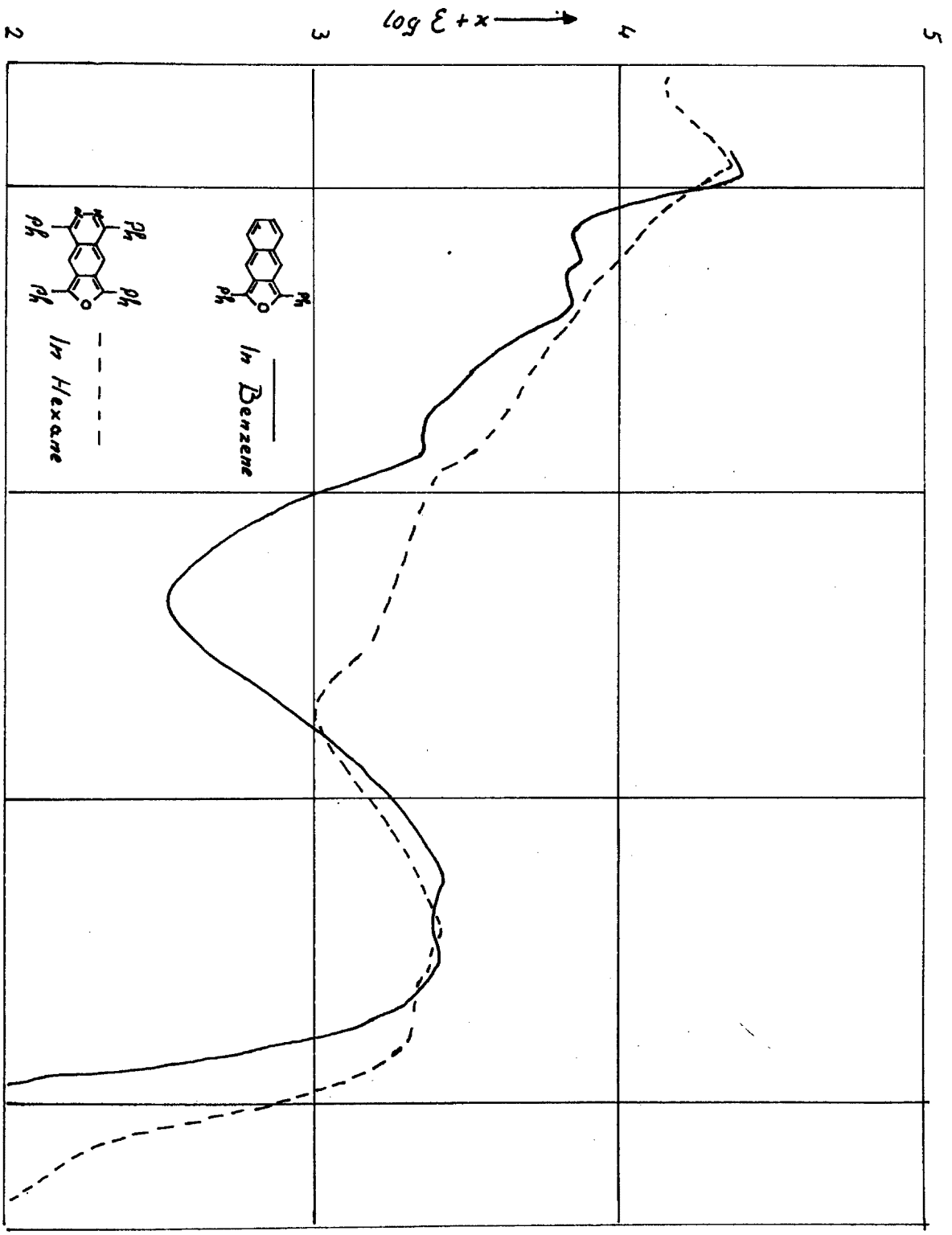
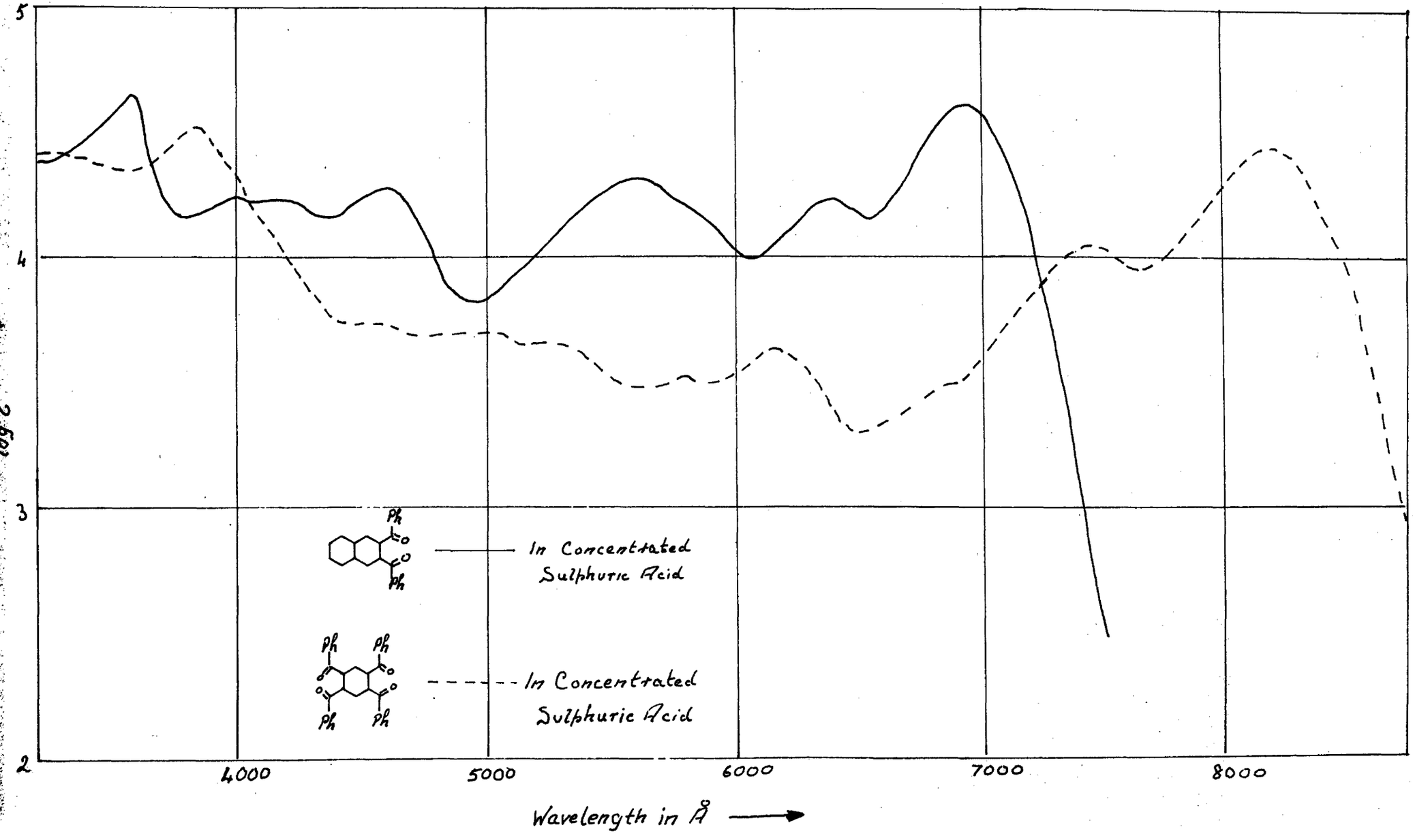

log ε + x
2
3
4
5
3000
4000
5000
6000
Wavelength in Å
In Benzene
In Hexane

Fig. IV


5
4
3
2
log ε
4000
5000
6000
7000
8000
Wavelength in Å
Ph
O
In Concentrated Sulphuric Acid
In Concentrated Sulphuric Acid

TETRACHLORODURENE, (28).

A stream of chlorine (5 bubbles per sec.) was passed through a solution of durene (50 g) in refluxing carbon tetrachloride, under irradiation from a mercury arc lamp, for 5 hours. After cooling, the crystallised, crude tetrachlorodurene was removed and chlorination continued for a further two periods of two hours. Recrystallisation from carbon tetrachloride gave tetrachlorodurene (26 g) m.p. 140-142° (Lit. 144°).

1,2,4,5 - TETRABENZYLBENZENE, (27).

a) Tetrachlorodurene did not condense with benzene at room temperature in the presence of anhydrous ferric chloride. Heating the mixture on a steambath initiated the reaction but no tetrabenzylbenzene could be isolated from the black tar produced.

b) A solution of tetrachlorodurene (7 g) in benzene was added to a 100% excess of phenyllithium in ether forming, by immediate exothermic reaction, a thick yellow precipitate. Decomposition with water and removal of the benzene by steam distillation left a yellow resin (12.5 g). Extraction with

methanol removed diphenyl (0.9 g) leaving insoluble yellow polymeric material (11 g).

c) A solution of phenylmagnesium bromide (bromobenzene (78.5 g) and magnesium (12.15 g)) in ether was treated with a solution of tetrachlorodurene (15 g) in dry benzene. After removal of the ether, the solution was refluxed for 2 hours. The mixture was decomposed with ice and dilute hydrochloric acid and the organic layer washed thoroughly with water. Concentration gave tetrabenzylbenzene (12.8 g) which crystallised from petrol (b.p. 100°-120°) as glistening needles, m.p. and mixed m.p. 140-141°. (Yields 60-65%.)

DEHYDROGENATION OF 1,2,4,5 - TETRABENZYLBENZENE.

Tetrabenzylbenzene was refluxed for 16 hours with an excess of chloranil in maleic anhydride, the only isolable product being chloranilic acid m.p. 282°.

1,2,4,5 - TETRABENZOYLBENZENE, (25).

Cromium trioxide (25 g), dissolved in the minimum amount of water, was added during 15 minutes to a refluxing solution of tetrabenzylbenzene (13 g)

in acetic acid (500 ml) and the refluxing continued for 26 hours. On cooling, tetrabenzoylbenzene (7.4 g) crystallised as colourless needles. Addition of water gave a further quantity of tetrabenzoylbenzene (2.6 g). Crystallisation from xylene gave colourless needles m.p. 258°. (Lit. m.p. 259-261°.) The diazine obtained from tetrabenzoylbenzene and hydrazine hydrate in acetic acid crystallised from dimethylformamide in yellow plates m.p. 407-8°.

REDUCTION OF 1,2,4,5 - TETRABENZOYLBENZENE.

Tetrabenzoylbenzene dissolved in concentrated sulphuric acid forming a neutral grey solution. On addition of copper powder this solution quickly became deep green. After filtration the solution was poured into acetic anhydride giving a greenish-blue solution whose absorption spectrum had bands at 3700 and 6300 Å, and which was unaffected by maleic anhydride.

REDUCTION OF 1,2,4,5 - TETRABENZOYLBENZENE TO 5,6 - DIBENZOYL-1,3-DIPHENYLISOBENZOFURAN (33).

A solution of tetrabenzoylbenzene (2 g) in concentrated sulphuric acid (100 ml) was stirred

with copper powder (5 g) for 5 minutes. After removal of the copper by filtration the green solution was poured into iced water and the greenish yellow precipitate collected. Crystallisation from benzene gave orange yellow needles m.p. 277-278° which dissolved in acetic anhydride with 1 drop of concentrated sulphuric acid to give a greenish blue solution. (Found: C,84.82; H,4.90. $C_{34}H_{24}O_3$ requires C,84.98; H,5.04. $C_{34}H_{22}O_3$ requires C,85.33; H,4.64%.) It had strong absorption peaks in the infra-red at 1645 and 1660 cms^{-1}.

MALEIC ANHYDRIDE ADDUCT, (37).

An excess of freshly distilled maleic anhydride in xylene, was added to a solution of 5,6-dibenzoyl-1,3-diphenylisobenzofuran (0.4 g) in xylene at 60°. The initial deposit of small prisms and warts, formed on cooling, was removed and, after standing for several days, the adduct crystallised from the filtrate in colourless prisms which became red at 220° and melted at 227-8°. (Found: C,79.73; H,5.00. $C_{38}H_{24}O_6$ requires C,79.16; H,4.19%.)

The adduct dissolved in dilute potassium hydroxide but, on standing, pure 5,6-dibenzoyl-1,3-

diphenylisobenzofuran (33) was precipitated. Dissociation also occurred in boiling xylene, the adduct being reformed as the solution cooled.

1,3,5,8 - TETRAPHENYL- 6,7 - DIAZA - (2',3') - ISONAPHTHOFURAN, (38).

Hydrazine hydrate (3 ml) was added to a solution of 5,6-dibenzoyl-1,3-diphenylisobenzofuran (0.3 g) in hot acetic acid (50 ml) and the deep bluish-green solution stirred for 1 minute. Precipitation with water gave a violet-blue powder (0.25 g) which could not be crystallised. (Found: N, 5.83. $C_{34}H_{22}N_2O$ requires N, 5.90%.)

MALEIC ANHYDRIDE ADDUCT OF (38).

An excess of maleic anhydride in xylene was added to a warm solution of 1,3,5,8-tetraphenyl-6,7-diazaisonaphthofuran (0.3 g) in xylene, the deep red colour being immediately discharged. Concentration gave the adduct which crystallised from benzene in small colourless prisms m.p. 300-305° dec. (Found: C,80.28; H,5.02. $C_{38}H_{24}O_4N_2$ requires C,79.70; H,4.23%.)

REDUCTION OF 1,2,4,5-TETRABENZOYLBENZENE TO 5:6-(2',3'DIPHENYL-(3':4')-TETRAHYDROFURANO)-1,3-DIPHENYLPHTHALAN (41).

Copper powder (5 g) was stirred with a solution of 1,2,4,5-tetrabenzoylbenzene (4 g) in concentrated sulphuric acid for two and a half hours. After filtration, this solution was poured into iced water (700 ml). The yellow-green precipitate was collected and dissolved in a large volume of benzene. On concentration, small pale yellow prisms (0.85 g) crystallised from the hot solution and on further concentration 5,6-dibenzoyl-1,3-diphenylisobenzofuran (0.32 g) was obtained. The double diphenylphthalan (41) crystallised from dichlorobenzene as pale yellow prisms, (m.p. 313-4° dec.) insoluble in cold concentrated sulphuric acid, but dissolving on heating giving a pale green solution. (Found: C,87.46; H,5.34. $C_{34}H_{26}O_2$ requires C,87.53; H,5.62%.)

On sublimation this material decomposed. The sublimate, a red oil, dissolved in benzene giving a magenta coloured solution with red fluorescence which had absorption bands at 5110,

5460 and 5910 Å. No pure compound, however, could be isolated, decomposition taking place on chromatography and exposure to light.

REDUCTION OF 1,2,4,5-TETRABENZOYLBENZENE.

1,2,4,5-Tetrabenzoylbenzene (2 g) was stirred with copper powder (3 g) in concentrated sulphuric acid for one and a quarter hours. Precipitation with water and crystallisation from benzene afforded 5,6-dibenzoyl-1,3-diphenylisobenzofuran (0.35 g). Concentration of the mother liquors gave a red oil from which no pure compound could be isolated. Maleic anhydride (5 g) and benzene (1 ml) were added to this oil and the mixture refluxed for 12 hours. When no adduct had crystallised after 6 days, water was added and the benzene removed by steam-distillation. The light brown powder (0.5 g) obtained was dissolved in a small volume of acetic anhydride, filtered (charcoal) and treated with sodium-dried ether, giving a grey powder which darkened at 235° and melted between 245 and 250°. (Found: C,76.56; H,4.33. $C_{42}H_{26}O_8$ requires C,76.59; H,3.98%.)

2,3-BISBROMOMETHYLNAPHTHALENE, (48).

2,3-Dimethylnaphthalene (20 g), N-bromosuccinimide (53 g) and benzoyl peroxide (0.35 g) were refluxed in dry carbon tetrachloride (150 ml) for 5 hours under irradiation by a mercury arc lamp. Filtration of the hot solution removed most of the succinimide. The crude product, deposited from the carbon tetrachloride on cooling, was extracted with hot benzene (250 ml), the solution washed with sodium hydroxide (5%), dried and concentrated. 2,3-Bisbromomethylnaphthalene (18.5 g, yield 46%) crystallised from benzene in large colourless prisms m.p. 150°. (Found: C,45.51; H,3.08. $C_{12}H_{10}Br_2$ requires C,45.89; H,3.21%.)

2,3-DIBENZYLNAPHTHALENE, (52).

a) A 100% excess of phenyllithium in ether was added to a solution of 2,3-bisbromomethylnaphthalene (10 g) in dry benzene forming, immediately, a heavy white precipitate. After refluxing for 10 minutes, the benzene and lithium bromide were removed by boiling with water leaving white, sparingly soluble, polymeric material (4.2 g).

b) A 100% excess of phenylmagnesium bromide in ether was added to a solution of 2,3-bisbromomethylnaphthalene (4 g) in benzene and, after removal of the ether, the mixture was refluxed for 30 minutes. The complex was decomposed with dilute acetic acid and the benzene layer washed and concentrated. 2,3-Dibenzylnaphthalene (2 g, yield 50%) crystallised from petrol (b.p.100-120°) in colourless needles, m.p. 139.5°. (Found: C,93.26; H,6.57. $C_{24}H_{20}$ requires C,93.46; H,6.54%.)

OXIDATION OF 2,3-DIBENZYLNAPHTHALENE.

a) 2,3-Dibenzylnaphthalene (0.2 g) and powdered selenium dioxide (0.15 g) were refluxed in ~~nitrogen~~ nitrobenzene for ten hours. The precipitated selenium was removed by filtration of the hot solution, and brown rods (70 mg) separated on cooling. Recrystallisation from xylene gave short light brown rods which softened at 288° and melted at 301°, and were soluble in concentrated sulphuric acid giving a violet solution with absorption bands at 613, 568, 529 mu. (Found: C,85.65; H,4.34. $C_{24}H_{16}O_2$ requires C,85.69; H,4.80%.)

b) 2,3-Dibenzylnaphthalene (0.35 g), selenium dioxide (0.28 g) and water (7 ml) were heated to 170° for 18 hours in a sealed tube. Addition of ether to a benzene extract precipitated a brown powder (0.1 g) which crystallised from benzene in short rods (15 mg) which were identical with those described above, (a).

c) 2,3-Dibenzylnaphthalene (0.35 g) and selenium dioxide (0.26 g) were refluxed for 18 hours in acetic acid (20 ml). Precipitation with water, extraction with xylene and concentration gave a tar which showed absorption at 1655 and 1720 cms^{-1} in the infra-red. This was boiled for 7 hours with potassium hydroxide (150 ml, 5%). The product crystallised from xylene in short brown rods identical with those described above, (a).

d) The oxidation product of 2,3-dibenzylnaphthalene (30 mg) was refluxed with zinc dust (170 mg) in acetic acid (2.5 ml) for 1¼ hours by which time the initial red colour had changed to yellow, the solution having a green fluorescence. Rapid chromatography of the product on grade I alumina, with benzene as eluent, gave a bright yellow solution with green fluorescence which had sharp absorption bands at 4830, 4530, 4280 and 4050 Å.

CONDENSATION OF 1,2-BISBROMOMETHYLBENZENE WITH Cis-DIBENZOYLETHYLENE.

Cis-Dibenzoylethylene (5 g) and zinc dust (1.5 g) in dimethylformamide were treated with 1,2-bisbromomethylbenzene (5 g) (as directed by Alder and Fremery[2]). The only products isolated, apart from a small quantity of insoluble material, were cis- and trans-dibenzoylethylene.

2,3-DIBENZOYLNAPHTHALENE (35).

Aqueous potassium hydroxide (0.5 ml, 5%) was added to a solution of o-phthalaldehyde (1.1 g) and diphenacyl (2 g) in ethanol (100 ml), and the temperature maintained at 50° for 10 minutes. On cooling, dibenzoylnaphthalene (2.05 g, 75%) separated. It crystallised from ethanol in colourless rods or prisms, m.p. 145°, which dissolved in concentrated sulphuric acid giving a deep green solution. (Found: C,85.67; H,4.82. Calculated for $C_{24}H_{16}O_2$: C,85.69; H,4.80%.)

The azine, m.p. 227°, was obtained by reaction with hydrazine hydrate in acetic acid.

REDUCTION OF 2,3-DIBENZOYLNAPHTHALENE.

Reduction of the diketone was accomplished readily with zinc dust in warm acetic acid with the production of a bright red solution with red fluorescence having absorption bands at 5280 and 5550 Å. Over-reduction occurred readily and terminating the reaction by addition of water gave only inseparable mixtures.

1,3-DIPHENYL-(2':3')-ISONAPHTHOFURAN (36).

Copper powder (0.5 g) was stirred into a solution of 2,3-dibenzoylnaphthalene (0.3 g) in concentrated sulphuric acid (50 ml) causing a colour-change from deep green to orange-yellow after 1 minute. After filtration, the solution was poured into iced water (500 ml) and the bright violet-red precipitate (0.25 g) collected with as little exposure to light as possible. All attempts to crystallise this material failed. Solutions of diphenylisonaphthofuran, protected from light, were readily reoxidised to 2,3-dibenzoylnaphthalene by exposure to the atmosphere; if not protected from light, photo-oxidation occurred rapidly. Solid

diphenylisonaphthofuran was stable in the absence of light.

MALEIC ANHYDRIDE ADDUCT (55).

To a solution of 1,3-diphenylisonaphthofuran (0.25 g) in benzene was added a benzene solution of freshly distilled maleic anhydride (0.5 g), causing immediate discharge of the bright red colour. Concentration, followed by steam-distillation of the remaining benzene, left a light brown resin which crystallised from petrol (b.p. 100-120°) in colourless silky needles, m.p. 236-7° (0.19 g, 58%). Found: C, 80.50; H, 4.16. $C_{28}H_{18}O_4$ requires C, 80.37; H, 4.34%.)

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